

LOW DIMENSIONAL MAGNETIC EXCHANGE IN VANADYL PYROPHOSPHATE
AND VANADYL HYDROGEN PHOSPHATE HEMIHYDRATE

By

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This thesis investigates the magnetic exchange in the material $(VO)_2P_2O_7$ and its deuterated precursor $VO(DPO_4) \cdot \frac{1}{2}D_2O$. The precursor material $VO(DPO_4) \cdot \frac{1}{2}D_2O$ is a simple antiferromagnetic dimer, but investigations on a triple axis neutron spectrometer reveal that the magnetic exchange does not occur along the previously expected V-O-V exchange path, but along the far longer V-O-P-O-V path through a PO_4 phosphate group. The material $(VO)_2P_2O_7$ has been proposed as the prototypical example of the Heisenberg antiferromagnetic two leg spin ladder, but that identification relied upon a lack of magnetic exchange along a V-O-P-O-V path nearly identical to that in the precursor material. Investigations of a powder of $(VO)_2P_2O_7$ on a triple axis neutron spectrometer reveal a previously undetected excitation that casts the material's identification as a spin ladder into doubt. Further investigations of an array of single crystals of $(VO)_2P_2O_7$ on a triple axis neutron spectrometer succeed in characterizing the dispersion of the material, and positively identify the magnetic properties as a one dimensional alternating dimer chain. Two modes are observed in the dispersion, with the origin of the upper mode remaining unidentified. Two explanations for the upper mode are presented.

CHAPTER 1

INTRODUCTION

The behavior of low-dimensional magnetic systems is of great interest in modern condensed matter physics. Systems such as the integer-spin Heisenberg antiferromagnetic chains¹, spin-Peierls systems², and spin ladders^{3,4} have all been shown to exhibit spin gaps. It has been suggested that spin ladders may exhibit superconductivity under doping.⁴ Alternating Heisenberg antiferromagnetic chains may exhibit a novel bound two magnon mode.⁵ This wide variety of behavior arises from very simple conceptual pictures, but is often driven by the quantum nature of the interaction.

These low-dimensional magnetic systems are of great interest for both practical and theoretical reasons. On the practical side, recent studies have suggested that two dimensional magnetism may play a significant role in high- T_c superconductivity⁶, thus stimulating considerable interest in these systems. The theoretical interest stems from the fact that these are quantum systems with a sufficiently simple Hamiltonian to admit the possibility of a full solution. The greater quantum fluctuations and lack of long range order in one dimensional systems often creates more complex solutions than in two or three dimensional systems.

Despite the simple appearance of the Hamiltonians, these systems exhibit complex and highly quantized behavior. Haldane¹ conjectured that a simple one dimensional magnetic chain would have a spin gap for all integer spins, but would be gapless for half-integer spins, a conjecture that has been backed up with considerable experimental evidence.⁷ An analogous situation has been found to exist in the quasi-one dimensional spin ladder configuration, in which ladders with an even number of legs would exhibit an energy gap, but ladders with an odd number of legs would not.

Vanadyl pyrophosphate ($(\text{VO})_2\text{P}_2\text{O}_7$, or VOPO for short) was proposed as an ideal candidate for a two-leg, spin- $1/2$ Heisenberg antiferromagnetic spin ladder⁸. However, some evidence exists supporting VOPO as a strictly one dimensional alternating chain of spins.⁹ Theoretical investigations into the two-leg spin ladder¹⁰ have been followed by inelastic neutron scattering studies of a powder of the material.¹¹ The investigations in this thesis used inelastic neutron scattering on both a powder¹² and a single crystal array,¹³ as well as a precursor material $\text{VO}(\text{DPO}_4) \cdot 1/2\text{D}_2\text{O}$.¹⁴ This thesis investigates the magnetic properties of VOPO to provide a final resolution to this question.

The basics of neutron scattering are discussed in Chapter 2. A basic theory of neutron scattering is developed, and forms for the structure factor and the magnetic structure factor are presented. The neutron spectrometers used for experiments presented in this thesis are also discussed individually.

In Chapter 3, the theory behind several low dimensional magnetic systems is discussed. Specifically, the expected dispersion and magnetic susceptibility is calculated for the isotropic and anisotropic forms of the magnetic dimer, alternating chain, and spin ladder. For the last two models, only the spin- $1/2$ cases are considered.

Chapter 4 considers the deuterated precursor to VOPO, vanadyl hydrogen phosphate hemihydrate ($\text{VO}(\text{DPO}_4) \cdot 1/2\text{D}_2\text{O}$, or VODPO). This material is a simple antiferromagnetic dimer, which allows the determination of the exact magnetic exchange path in the material. The structural similarities to VOPO can be used to provide insight into the magnetic exchange in VOPO as well.

Chapter 5 concerns experiments on a powder sample of VOPO. An excitation not predicted by theory is discovered, and its implications for both the spin ladder and alternating chain models are discussed.

Chapter 6 examines an aligned array of single crystals of VOPO. The dispersion of the material is measured in each crystal direction. The dispersion is compared to the

predictions of the spin ladder and alternating chain models, allowing a determination of VOPO's magnetic structure. The differences between the measured and predicted dispersions are discussed along with their implications.

The thesis concludes with a discussion of further experiments that can resolve the remaining questions about magnetic exchange in VOPO, as well as avenues for continuing theoretical work on low dimensional magnetic exchange.

CHAPTER 2

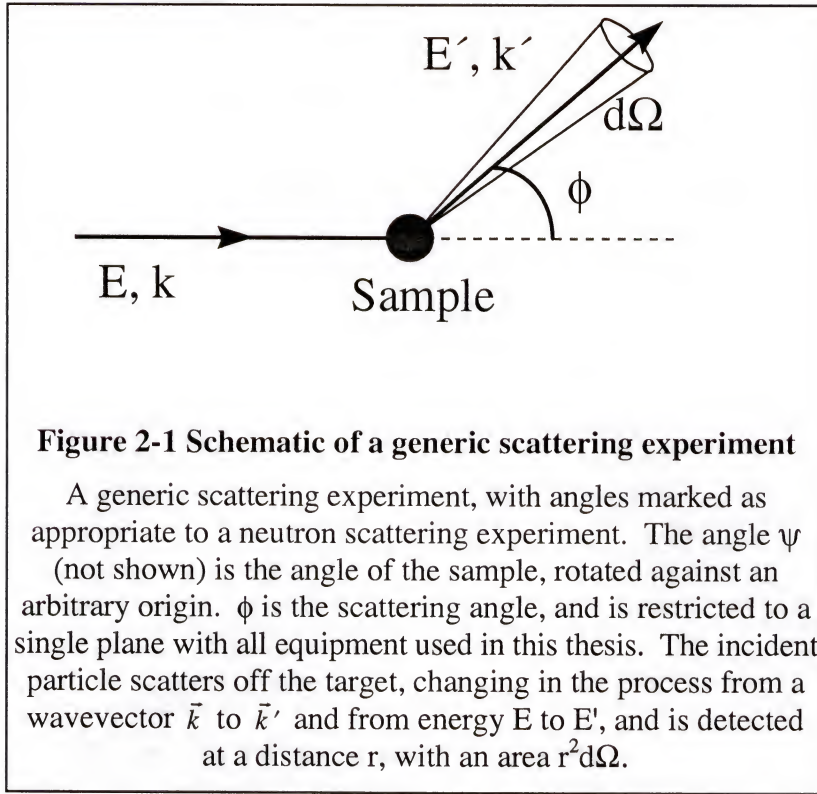
THEORY OF NEUTRON SCATTERING

Neutron scattering is a powerful tool for investigating the magnetic, dynamic, and structural properties of materials. It is the principal technique used in this thesis to examine the magnetic properties of $(\text{VO})_2\text{P}_2\text{O}_7$. The goal of a neutron scattering experiment is to extract information about the structure factor, $S(\vec{k}, \omega)$, for the material.

In this chapter, the methods of examining the structure factor through neutron scattering are examined, building from the general to the specific. First, a generic scattering experiment applicable to any scattered particle is examined. The next section relates the scattered intensity to the structure factor in neutron scattering specifically. The structure factor itself is examined in the third section, in its magnetic and non-magnetic forms. The chapter concludes by examining the neutron scattering facilities used in this thesis.

2.1 Generic Scattering Experiments

Scattering is a common technique for determining the properties of materials. A scattering experiment consists of hitting a sample with an incoming beam of scattering particle, then measuring the outgoing intensity of particles at different locations. The scattering particles can be light, x-rays, electrons, neutrons, or almost any other type of particle, with each different particle making different information about the sample available, depending on how it interacts with the sample. A generic form for the scattered intensity is developed in this section, independent of either particle or sample.



A generalized scattering experiment is displayed in Figure 2-1. The scattering particle is incident on the target with a wavevector $\vec{k} = 2\pi\lambda^{-1}$. In general, it leaves the target with a new direction, and wavevector $\vec{k}' = 2\pi\lambda'^{-1}$, scattering into the solid angle $d\Omega$, and detected over the area $r^2 d\Omega$. The scattering vector is defined as $\vec{\kappa} = \vec{k}' - \vec{k}$, with energy transfer $\hbar\omega = \hbar^2(2m)^{-1}(k'^2 - k^2)$. These two quantities are not independent, which may place kinematic restrictions on the energy change observable for a given momentum transfer.

The measured quantity in a scattering experiment is the differential cross section, which gives the fraction of incident particles with energy E scattered into solid angle Ω with energy E' . In the case of elastic scattering, where $E = E'$, it has been shown¹⁵ that the cross section is

$$\frac{d\sigma}{d\Omega} = \left| \langle \vec{k}' | \hat{V} | \vec{k} \rangle \right|^2 \quad (2-1)$$

where V is the interaction potential that causes the transition of the scattering particle from wavevector $\vec{k}$ to $\vec{k}'$.

In inelastic scattering, the scattering particle changes both its wavevector $\vec{k}$ and energy ω . The target will also change its state in such a case, which is labeled as a change from state λ to state λ' . Conservation of energy will require that $\hbar\omega = E_{\lambda'} - E_{\lambda}$. A normalization factor is also required for the incoming and outgoing particles. In full, the differential cross-section is¹⁵

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\lambda'}^{\lambda} = \frac{k'}{k} \left| \langle \vec{k}' \lambda' | \hat{V} | \vec{k} \lambda \rangle \right|^2 \delta(\hbar\omega + E_{\lambda} - E_{\lambda'}) \quad (2-2)$$

where $\vec{k}$ and $\vec{k}'$ are the initial and final wavevectors of the scattered particles, E_{λ} and $E_{\lambda'}$ are the initial and final energies of the system in states λ and λ' , V is the interaction potential, and $\hbar\omega$ is the change in energy of the scattered particle. However, this cross section relates to specific initial and final states of the target, when in general, there will be a range of states available, requiring a weighted average over those states. A more general form then, is¹⁶

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\lambda'}^{\lambda} = \frac{k'}{k} \sum_{\lambda, \lambda'} p(\lambda) \left| \langle \vec{k}' \lambda' | \hat{V} | \vec{k} \lambda \rangle \right|^2 \delta(\hbar\omega + E_{\lambda} - E_{\lambda'}) \quad (2-3)$$

where $p(\lambda)$ is the probability of the sample being in an initial state λ , and all other variables defined as in Equation (2-2).

Other averages may also come into effect in this calculation, depending upon the nature of the scattering experiment. For instance, a powder sample requires a powder average over all orientations, and neutron scattering requires an average over all possible spin states.

2.2 Interaction Potentials In Neutron Scattering

Neutron scattering, specifically, has two major advantages over most other forms of scattering, due to the nature of its interaction with matter. First, the energies involved in neutrons are typically on the same scale as dynamic and magnetic excitations in matter. Second, neutrons have minimal interaction, due to their neutral charge, which allows them to be used as a probe of bulk behavior. These two advantages, along with some difficulties arising from them, are discussed in this section.

First, the energies of neutrons can be characterized in several equivalent ways, by

$$E_n = \hbar\omega = k_B T = \frac{h^2}{2m\lambda^2} \quad (2-4)$$

which allows the energy to be quoted by its frequency ω , its temperature T , or its wavelength λ , where m is the mass of the neutron, h is Plank's constant, and k_B is

Table 2-1 Energy and Wavelength of Thermal Neutrons

T	100 K	300 K	500 K
E (meV)	8.6	25.8	43.1
λ (Å)	3.08	1.78	1.37

Boltzmann's constant. Neutron energies available today range from roughly 1 μ eV to 1 eV, although no single spectrometer handles the entire range.

One useful range of neutron energies, used in this thesis, is known as "thermal neutrons", obtained by thermalizing the neutrons from a reactor in water, producing a Maxwellian distribution of neutron energies centered roughly around 300K. The energies and wavelengths of neutrons in the thermal range are shown in Table 2-1. In general,

excitations in matter are ~ 10 meV, while atomic separations are ~ 1 Å. The energies and wavelengths of thermal neutrons are on that scale in both cases.

While the properties of the neutrons are important, their interaction with the sample is of equal importance. The nucleon-nucleon interaction is complex, but also very short range, on the order of 10^{-5} Å.¹⁵ Because this is considerably less than the wavelength of thermal neutrons, the scattering can contain only s-wave, isotropic, components.¹⁵ The Fermi pseudo-potential can therefore be used to represent the interaction potential of the system

$$V(\vec{r}) = \frac{2\pi\hbar^2}{m} b\delta(\vec{r} - \vec{R}) \quad (2-5)$$

where b is defined as the scattering length of the atom, and is positive for an impenetrable sphere of radius b . The scattering length b can be complex, in which case the imaginary part of b represents the absorption of the atom, the real part scattering. In the remainder of the discussion, only the real portion of b is considered.

This pseudo-potential allows a great simplification, by breaking the scattering length itself into smaller parts. The cross-section from a rigid array of atoms, each with the Fermi pseudo-potential, must be elastic (if the array is fully rigid), and so, substituting the potential of Equation (2-5) into the scattering cross-section of Equation (2-1),

$$\frac{d\sigma}{d\Omega} = \sum_{ll'} \exp(i\vec{\kappa} \cdot (\vec{R}_l - \vec{R}_{l'})) \overline{b_{l'}^* b_l} \quad (2-6)$$

where l and l' are sites of atoms in the array.¹⁵ The values of b are not correlated between different atoms, when $l \neq l'$, but are clearly correlated when $l = l'$. In general, then¹⁷,

$$\overline{b_{l'}^* b_l} = |\overline{b}|^2 + \delta_{ll'} \left(|\overline{b}|^2 - |\overline{b}|^2 \right) \quad (2-7)$$

where $\bar{b}$ is the average of the scattering lengths over all the atoms in the matrix, allowing the cross-section to be written as¹⁵

$$\frac{d\sigma}{d\Omega} = \left(\frac{d\sigma}{d\Omega} \right)_{\text{coh}} + \left(\frac{d\sigma}{d\Omega} \right)_{\text{incoh}} \quad (2-8)$$

in other words, as a coherent and incoherent part. In this same manner, the scattering length is divided into a coherent and incoherent length.

This breakdown represents qualitatively different types of scattering. The coherent amplitude is based on the average scattering length, and comes from interference by many atoms in the array. The incoherent amplitude has no interference, and comes from individual atoms. In the case of a fully rigid array, the incoherent scattering is also completely isotropic.¹⁶

While the equations given above were derived for a fully rigid array of atoms, the breakdown of the scattering cross section into coherent and incoherent parts applies very well to real crystals, where the atomic vibrations are small compared to the interatomic distances. The incoherent scattering derived from a fully rigid array is isotropic, while in a real crystal it is slightly anisotropic, typically by less than 5% of the incoherent scattering¹⁷.

There is currently no theory in place to determine the scattering length of an atom. Differing isotopes or even different spins of the same isotope can have greatly different scattering lengths, even changing sign in many cases. This can be a strength in some cases. For example, the scattering length of deuterium is $b = 0.67 \times 10^{-12} \text{cm}$, while hydrogen has a scattering length $b = -0.38 \times 10^{-12} \text{cm}$, allowing neutron scattering of liquid solutions in water to use a mixture of regular and heavy water to make the water transparent to neutrons, with a high amount of incoherent scattering being the primary drawback to this technique. Vanadium, for another example, scatters almost entirely incoherently, in a ratio of coherent : incoherent of 1:150, due to the ratio of the scattering length for its one stable

isotope between the + and - spin states, which makes it an ideal container to hold a sample in a diffraction experiment, for example, but causes difficulties if it is the target under investigation.

The largest disadvantage to neutron scattering is the low intensity of scattered neutrons. The same minimal interaction that makes neutrons such an ideal probe of bulk properties carries with it the problem of minimal scattering. Considerable effort has gone in to improving the incident flux, through design of the nuclear reactors, beam guides, and detection and shielding equipment, to provide one possible solution to that problem. The second solution to this problem is to provide samples that are large in comparison to those needed for most other techniques. A larger sample clearly has a greater probability of experiencing neutron interaction than a smaller sample.

2.3 Determination Of The Structure Factor From Neutron Scattering

Neutron scattering aims to extract the structure factor $S(\vec{\kappa}, \omega)$ for the sample being examined. Section 2.3.1 examines the structure factor when there are no magnetic interactions, while section 2.3.2 considers the structure factor with magnetic interactions. It will be shown that the two cases can be considered independently for an unpolarized neutron beam.

2.3.1 Scattering from non-magnetic structures

The ultimate aim of neutron scattering, like most other forms of scattering, is to obtain the dynamic structure factor, $S(\vec{\kappa}, \omega)$, which is the Fourier transform of the lattice structure and dynamics. The cross section for scattering from N particles can be written as¹⁵

$$\frac{d^2\sigma}{d\Omega dE'} = N \frac{k'}{k} \overline{|V_j(\vec{\kappa})|^2} S(\vec{\kappa}, \omega) \quad (2-9)$$

where $V_j(\kappa)$ is the Fourier transform of the potential from the j^{th} atom site. In this form, the structure factor is¹⁶

$$S(\vec{\kappa}, \omega) = \frac{1}{2\pi\hbar N} \int_{-\infty}^{\infty} \exp(-i\omega t) \sum_{jj'} \left\langle e^{(-i\vec{\kappa} \cdot \vec{R}_j)} e^{(i\vec{\kappa} \cdot \vec{R}_{j'}(t))} \right\rangle dt \quad (2-10)$$

where $\vec{\kappa}$ is the change in momentum of the neutron, and $\vec{R}_j$ and $\vec{R}_{j'}$ are the locations of atoms in the sample.

Equation (2-9) is important, because it is $S(\vec{\kappa}, \omega)$ that is actually desired from an experiment. Since the incoherent scattering is nearly isotropic in the experiments described in this thesis, it can be subtracted from the data as a constant background, leaving only the coherent scattering to be considered. The coherent scattering cross section is¹⁵

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{coh} = N \frac{k'}{k} \frac{\sigma_c}{4\pi} S(\vec{\kappa}, \omega) \quad (2-11)$$

where $\sigma_c = 4\pi |V(\vec{\kappa})|^2$ is the total cross section from coherent scattering only. This cross section can itself be broken down into elastic and inelastic components. For bulk samples, we find that¹⁵

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega} \right)_{coh}^{el} &= \frac{\sigma_c}{4\pi} \left| \int e^{(i\vec{\kappa} \cdot \vec{r})} \langle \rho(\vec{r}) \rangle d\vec{r} \right|^2 \\ \left(\frac{d^2\sigma}{d\Omega dE'} \right)_{coh}^{inel} &= \frac{N\sigma_c}{4\pi} \frac{k'}{k} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{(-i\omega t)} dt \int e^{(i\vec{\kappa} \cdot \vec{r})} G(\vec{r}, t) d\vec{r} \end{aligned} \quad (2-12)$$

where $G(\vec{r}, t)$ is the pair correlation function.

2.3.2 Scattering from magnetic systems

Scattering of neutrons depends not only on the scattering wavevector κ , but also on the orientation of the neutron spin $\vec{s}_n$ relative to the atomic spin $\vec{S}$. In order to represent this, the effective potential the neutron sees from the array of atoms will now be

$$V(\vec{\kappa}) = \frac{2\pi\hbar^2}{m} \sum_l b_l \exp(-i\vec{\kappa} \cdot \vec{R}_l) - \dots \quad (2-13)$$

$$- 2r_0\gamma \sum_l f_l(\vec{\kappa}) \exp(-i\vec{\kappa} \cdot \vec{R}_l) \left[|\vec{S}_l| |\vec{s}_n| - (\vec{e} \cdot \vec{s}_n)(\vec{e} \cdot \vec{S}_l) \right]$$

where r_0 is the electromagnetic radius of an electron, γ is the magnetic moment of the neutron, $f_l(\kappa)$ is the Fourier transform of the atomic form factor of the l^{th} atom, and $\vec{e}$ is the unit vector in the direction of $\vec{\kappa}$.¹⁸ The second term in Equation (2-13) is the contribution from the magnetic scattering, while the first term is the Fourier transform of Equation (2-5).

This potential can be used directly in all the expressions given in Equations (2-9) and following for neutron scattering. For an unpolarized neutron beam, however, there is a great simplification available. The interference term in $V(\vec{\kappa})^2$ becomes 0 when averaging over neutron spins, and so the resulting cross section becomes additive. It is therefore possible to treat magnetic and atomic scattering separately.

It is convenient to introduce a magnetic structure factor $F(\vec{\kappa})$, such that

$$\vec{F}(\vec{\kappa}) = \sum_l e^{(-i\vec{\kappa} \cdot \vec{R}_l)} \vec{S}_l f_l(\vec{\kappa}) \quad (2-14)$$

Using this, the magnetic cross section can be written as¹⁹

$$\begin{aligned}
\left(\frac{d^2 \sigma}{d\Omega dE} \right)^{mag} &= (r_0 \gamma)^2 \frac{k_f}{k_i} \sum_{\alpha, \beta} (\delta_{\alpha\beta} - \hat{\kappa}_\alpha \hat{\kappa}_\beta) \sum_{j'j} \left| \frac{g}{2} \vec{F}(\vec{\kappa}) \right|^2 * \dots \\
&* \sum_{\lambda_i \lambda_f} p(\lambda_i) \langle \lambda_i | e^{-i\vec{\kappa} \cdot \vec{R}_{j'}} S_{j'}^\alpha | \lambda_f \rangle \langle \lambda_f | e^{i\vec{\kappa} \cdot \vec{R}_j} S_j^\beta | \lambda_i \rangle * \dots \\
&* \delta(E_{\lambda_i} - E_{\lambda_f} + \hbar\omega)
\end{aligned} \tag{2-15}$$

where S_j^α is the α component of the spin at site j . $\delta_{\alpha\beta}$ is a Kronecker delta, and the product of the components of unit scattering vectors along the spin component directions subtracted from it ensure that only spin components perpendicular to the scattering wavevector κ contribute.

Equation (2-15) can be written in a more compact form,¹⁹

$$\frac{d^2 \sigma}{d\Omega dE_f} = \sigma_{mag} N \frac{k'}{k} \left(\frac{g}{2} \vec{F}(\vec{\kappa}) \right)^2 e^{-2W(\vec{\kappa})} \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\kappa}_\alpha \hat{\kappa}_\beta) S^{\alpha\beta}(\vec{\kappa}, \omega) \tag{2-16}$$

where σ_{mag} is a numerical constant including the relevant terms, and $\sigma_{mag} = 0.2896$ barns. The factor $\exp(-2W(\kappa))$ is the Debye-Waller factor, which falls off less rapidly than the magnetic form factor, and so is often neglected in considering magnetic scattering. The structure factor tensor is defined by

$$S^{\alpha\beta}(\vec{\kappa}, \omega) = \frac{1}{2\pi\hbar N} \sum_{jj'} e^{i\vec{\kappa} \cdot (\vec{R}_j - \vec{R}_{j'})} \int_{-\infty}^{\infty} e^{-i\omega t} \langle S_{j'}^\alpha(0) S_j^\beta(t) \rangle dt \tag{2-17}$$

In the cases in which the total z-component of the spin is a conserved quantity, as in the Heisenberg model, the off-diagonal components of the correlation function $S^{\alpha\beta} = 0$, when $\alpha \neq \beta$. The x and y axes are also equivalent in such a case, so $S^{xx} = S^{yy}$.¹⁵

2.4 Neutron Spectrometer Configurations

Four neutron spectrometers were used in the course of these investigations, and they will be described in this section. All the spectrometers were at the High Flux Isotope Reactor at Oak Ridge National Laboratory. The HB4 neutron diffractometer is discussed

first, followed by the HB1A two-axis spectrometer. The final spectrometers discussed are the HB1 and HB3 triple axis spectrometers.

2.4.1 HB4 spectrometer configuration

The HB4 spectrometer has been designed for use in analyzing powder samples. It

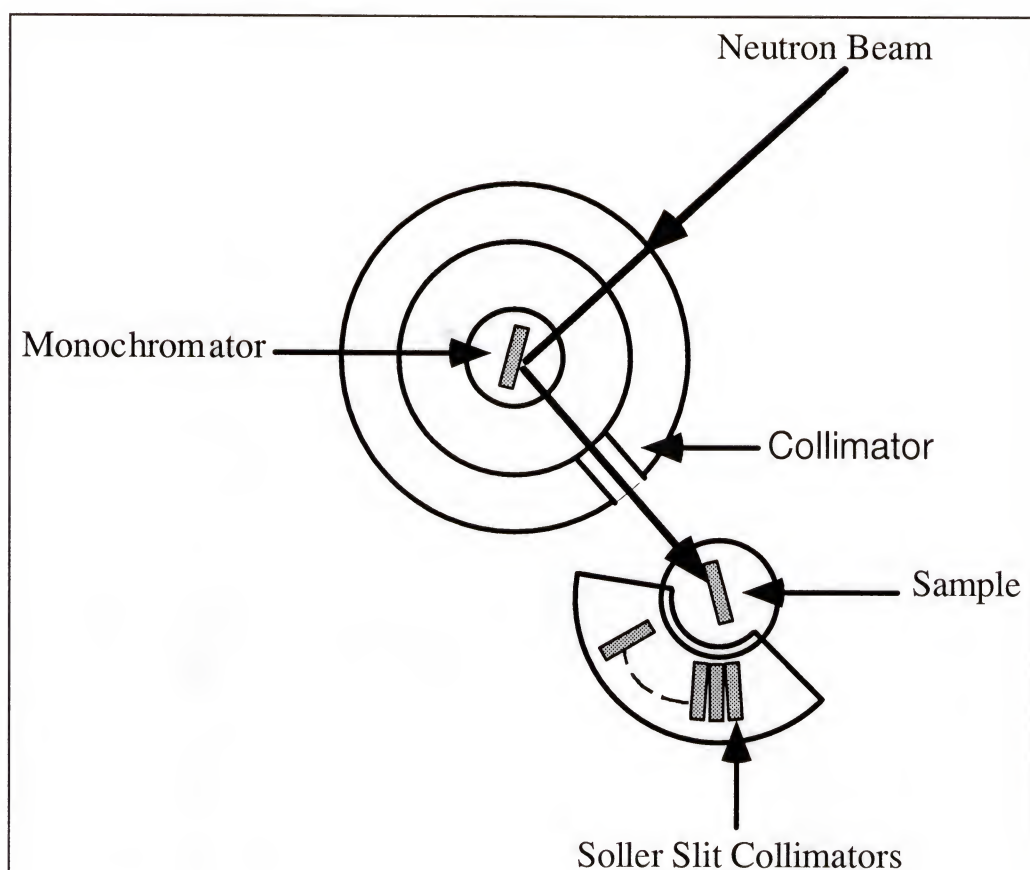


Figure 2-2 HB4 Spectrometer Schematic²⁰

The HB4 spectrometer hits the sample with a monochromatic neutron beam, which is then detected separately after each of an array of Soller Slit Collimators. There is no analyzer after the sample.

is a diffractometer, designed to scan a maximum range of angles. A diffractometer, there

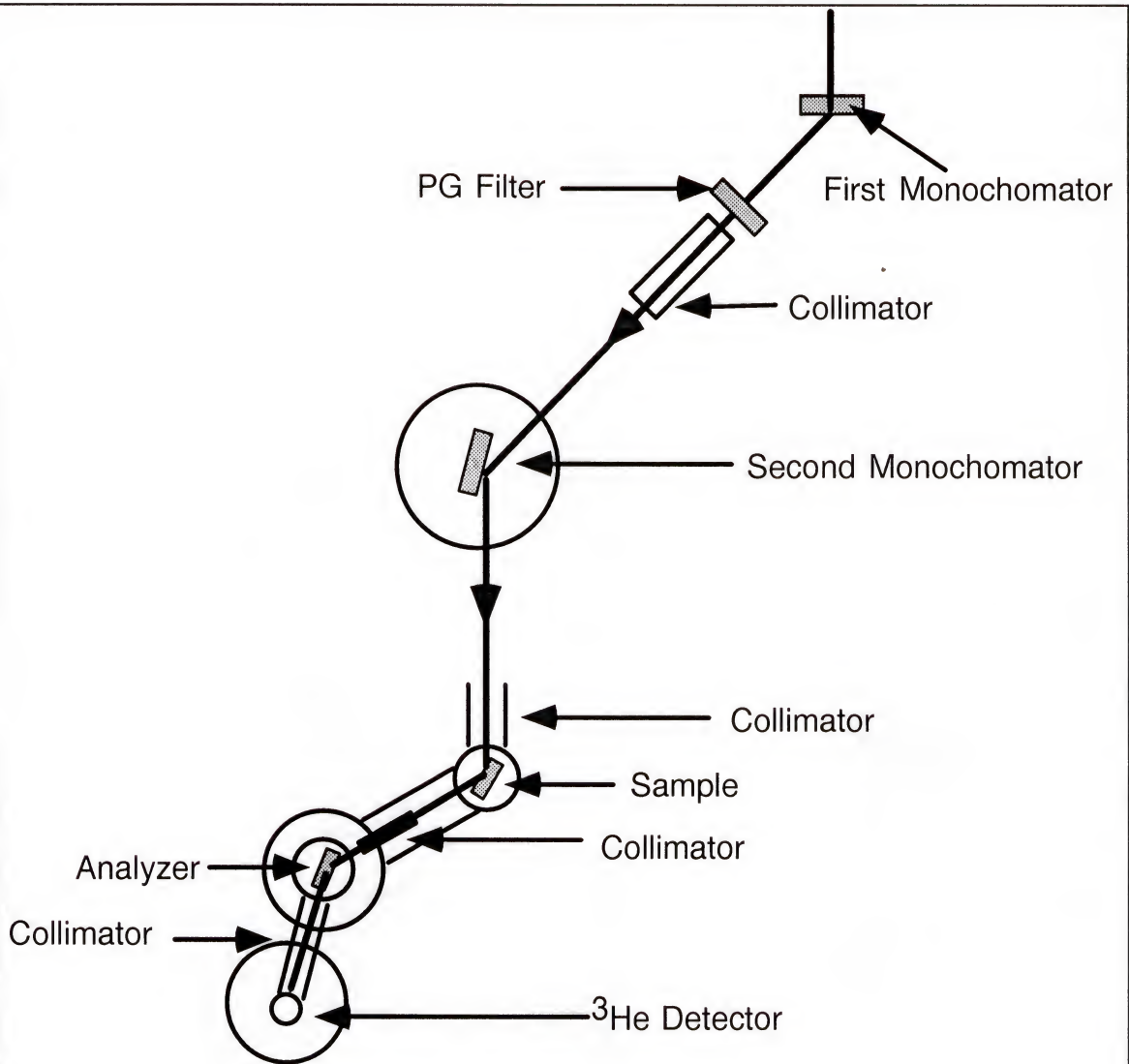


Figure 2-3 HB1A Spectrometer Schematic²⁰

The HB1 spectrometer consists of two fixed monochromators, giving a fixed initial energy of 14.7 meV. The sample and analyzer angles can be independently rotated.

is no analyzer before the detector, so the full range of scattered energy neutrons is observed at the detector. A schematic of the spectrometer is shown in Figure 2-2.

The diffractometer is measuring the quantity

$$\frac{d\sigma}{d\Omega} = N \frac{k'}{k} \frac{\sigma}{4\pi} \int S(\vec{\kappa}, \omega) d\omega$$

(2-18)

where σ is the scattering cross-section of the target. This measures the integral of the structure factor over energy. In general, though, the inelastic components are small compared to the elastic components.

The neutron beam in the HB4 spectrometer scatters off the sample into an array of 32 detectors, each with a Soller slit collimator in front of it. Each detector is separated from the next by 3.6° , covering a total of 115° . Therefore the entire range can be effectively scanned by moving only 3.6° . The detector banks are situated immediately behind the collimators.

2.4.2 HB1A spectrometer configuration

The HB1A spectrometer is a fixed incident energy spectrometer, and the details of the machine are shown in Figure 2-3.

A neutron beam used at fixed incident, instead of fixed final, energy, must be normalized for density of states, a factor of $k'k^{-1}$. This factor has been taken into account in all diagrams shown in this thesis.

2.4.3 HB1 and HB3 spectrometer configuration

The HB1 and HB3 spectrometers are a triple-axis spectrometers, with variable incident and final neutron energy. The HB1 spectrometer is capable of polarizing the neutron beam, although that capability was not used in any experiment in this thesis. A schematic of the HB1 spectrometer is shown in Figure 2-4. The HB3 spectrometer is the same as the HB1 spectrometer, except that it does not have a spin-flipper.

The energy of the neutron beam can be selected by varying the monochromator angle. The beam then scatters from the sample onto an analyzer crystal. By varying the analyzer angle, the final energy of the beam can be varied, allowing inelastic measurements. There are collimators before the monochromator, before the sample, after

the sample, and after the analyzer. This allows adjustment of the resolution for different experiments.

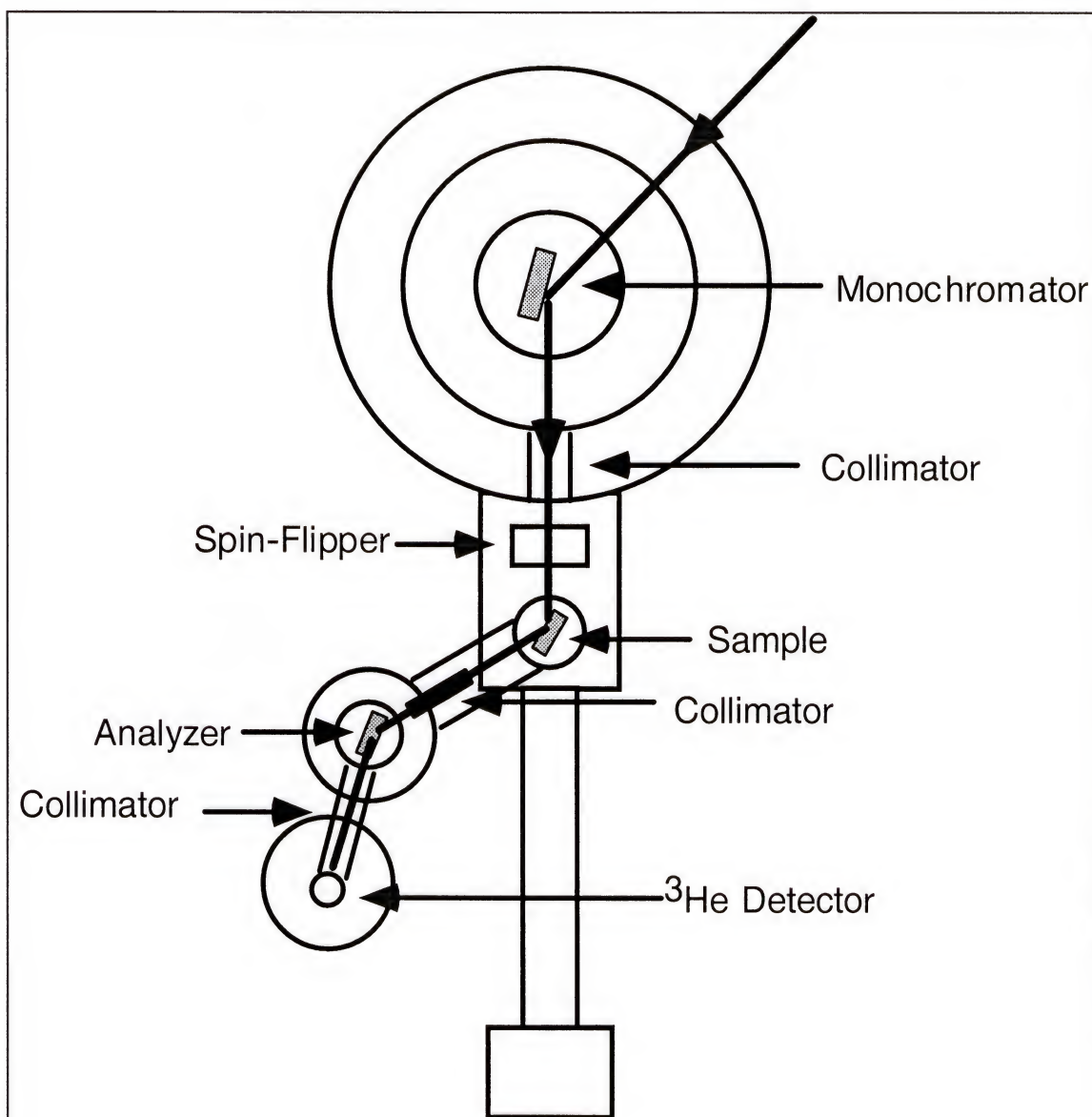


Figure 2-4 HB1 Spectrometer Schematic²⁰

The HB1 spectrometer hits the sample with a monochromatic neutron beam, which is reflected from the sample onto an analyzer before reaching the detector. Monochromator, sample, and analyzer angles are all independently adjustable.

CHAPTER 3

INTRODUCTION TO LOW-DIMENSIONAL MAGNETIC EXCHANGE SYSTEMS

This chapter examines the theory of some specific low-dimensional magnetic exchanges that occur in $(\text{VO})_2\text{P}_2\text{O}_7$ and $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$. The first section, 3.1, is an introduction to general magnetic exchange in condensed matter. Magnetic ordering and spin-spin interactions are discussed along with some methods of approximating their solution. Specific forms of magnetic exchange are discussed in sections 3.2, 3.3 and 3.4, beginning with a simple magnetic dimer, followed by an alternating chain, and concluding with the spin ladder. In each case, a dispersion relation and the magnetic susceptibility are developed, using a pseudo-boson approximation.

3.1 Introduction To Magnetism

Magnetic phenomena in materials containing ions with permanent magnetic moments take a wide variety of forms. Spin polarization and the Pauli Exclusion Principle are the primary cause of the variety of behavior. The total angular momentum in an atom, $\vec{J} = \vec{L} + \vec{S}$, includes contributions from the orbital angular momentum of electrons, $\vec{L}$, and spin, $\vec{S}$. However, in some transition metals, as with the V^{4+} ions in both $(\text{VO})_2\text{P}_2\text{O}_7$ and $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$, the outer shell is occupied by a single electron, $3d_1$, and the inner shells are filled, resulting in total spin $\frac{1}{2}$. The orbital momentum is often quenched by the crystal field in such cases²¹, resulting in 0 orbital momentum. The ions, in those cases, can be characterized by spin-only interactions.

3.1.1 Magnetic exchange and long range ordering

Magnetic materials undergo ordering at sufficiently low temperatures. The two simplest forms of ordering in a material are ferro- and antiferro-magnetic, in which

neighboring magnetic moments align along the same or opposite directions. Heisenberg proposed²² that the interaction between adjacent ions could be explained by the overlap of electronic shells and the Exclusion Principle. For neighboring ions, the exchange energy could be written

$$E = E_0 - 2J\vec{S}_1 \cdot \vec{S}_2 \quad (3-1)$$

where E_0 is a constant energy term, J is the exchange integral over electrostatic interactions, and $\vec{S}_1$ and $\vec{S}_2$ are the spins of the neighboring ions. For $J > 0$ this results in a ferromagnetic ordering. Antiferromagnetic ordering can come from indirect exchange²³, in which the exchange is moderated by a non-magnetic ion, a process known as magnetic superexchange. That arrangement can favor an antiferromagnetic ordering.

For negative values of J in Equation (3-1), the antiferromagnetic ordering of adjacent spins is energetically favored. Néel proposed²⁴ that a real three-dimensional solid that could be divided into magnetic sublattices would adopt a long range ordered antiferromagnetic state below a certain temperature, known as the Néel temperature, T_N . However, Bethe showed²⁵ that for a one-dimensional array of spins, the quantum fluctuations in the spins would prevent the formation of a long-range antiferromagnetically ordered state at any temperature.

3.1.2 Spin-wave approximation methods

The quantum mechanical theory of antiferromagnets has a serious difficulty in determination of the ground state. Two approximation methods that have been used with some success in examining one-dimensional antiferromagnets will be examined, the classical spin wave theory, and a pseudo-boson approximation.

A state with spins arranged in an antiparallel fashion, called the Néel state²⁴, does not correspond to the minimum energy of the interacting spins for a one-dimensional

system, and such a state may not even exist at all. Specifically, in the case of a Heisenberg Hamiltonian

$$\hat{H} = \sum_{j>k} J_{jk} \vec{S}_j \cdot \vec{S}_k \quad (3-2)$$

where J_{jk} is the nearest-neighbor exchange integral between sites j and k (note J has the opposite sign from Equation (3-1) for convenience), the total z component of spin is

$$S_z^{tot} = \sum_j (\vec{S}_j)_z \quad (3-3)$$

where the sum is over all spin sites. S_z does not commute with the Hamiltonian, and so cannot be an integral of motion, which rules out the Néel state, with its constant $S_z = 0$.¹⁶

The classical spin wave approximation treats the Néel state as the ground state of the antiferromagnet despite the problems. The spins are treated as two separate sublattices, one with spin up, one with spin down, so

$$\Psi = \prod_j \psi_j(+S) \prod_k \psi_k(-S) \quad (3-4)$$

is the product of the individual wavefunctions in the two sublattices. Anderson²⁶ used this approach to show that the Néel state is a good approximation in two and three dimensions, but it fails in one dimension, in which the assumption of long-range order collapses.

Another approximation scheme, known as the pseudo-Boson approximation, arises from the Tomonaga model²⁷ of a one-dimensional electron gas. The excitation spectrum of two fermions has boson-like properties, and the approximation is to treat the excitations as coming from bosons. This approach takes account of local spin fluctuations, but still keeps long-range order in the system.

The two-fermion excitation that forms the basis of the pseudo-boson model is identical to the magnetic dimer. The operators used in the pseudo-boson approximation are developed in section 3.2, along with the discussion of the magnetic dimer.

3.2 Dispersion And Susceptibility Of Magnetic Dimers

Magnetic dimers are one of the simplest magnetic systems available. A dimer is just two sites coupled magnetically, and isolated from any other sites. More complex systems can often be built up starting with dimers, especially if the inter-dimer coupling is weak compared to the dimer coupling. The dimer is an important picture in this thesis for both reasons. $\text{VO}(\text{HPO}_4) \cdot \frac{1}{2}\text{H}_2\text{O}$ is a simple dimer system, while in $(\text{VO})_2\text{P}_2\text{O}_7$, dimers are a useful starting point from which to build the more complex interactions.

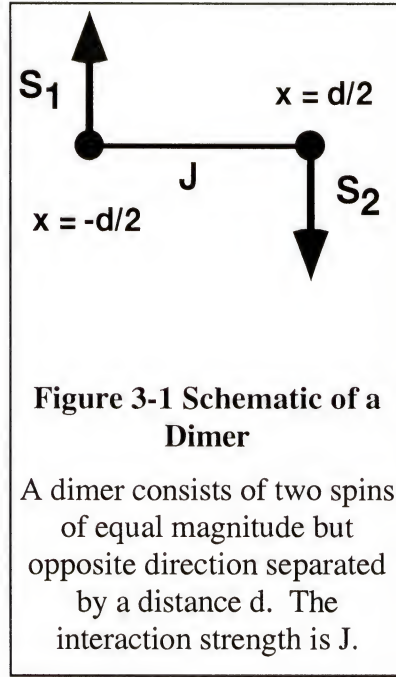
This section examines the magnetic dimer, and develops the pseudo-boson operators used in the pseudo-boson approximation for the more complex alternating chain and spin ladder models. The magnetic dimer is first described, and a Hamiltonian for the isotropic and anisotropic case is presented. The eigenfunctions and energy eigenvalues of the dimer are shown, and the operators used in the pseudo-boson approximation are shown. In sections 3.2.2 and 3.2.3, the structure factor and dispersion are calculated, followed by a calculation of the magnetic susceptibility of a dimer substance.

3.2.1 Description and Hamiltonian of a magnetic dimer

The Heisenberg antiferromagnetic isotropic dimer (referred to as a dimer system for short), consists of two atoms coupled antiferromagnetically, and can be represented by the Hamiltonian

$$H = J(\vec{S}_1 \cdot \vec{S}_2) \quad (3-5)$$

where J is the coupling strength, and $J > 0$. $\vec{S}_1$ and $\vec{S}_2$ are the spins of the two coupled atoms. With $J > 0$, it is immediately clear that the system has minimum energy when $\vec{S}_1$



and $\vec{S}_2$ are aligned in opposite directions. Schematically, the dimer system is represented in Figure 3-1.

It is possible to introduce anisotropy into the dimer, creating the Heisenberg antiferromagnetic anisotropic dimer (or anisotropic dimer for short), represented by the Hamiltonian

$$H = J \left(S_{1z} S_{2z} + \frac{\alpha}{2} (S_1^+ S_2^- + S_1^- S_2^+) \right) \quad (3-6)$$

here, again, $J > 0$ is the coupling strength, and $\vec{S}_1$ and $\vec{S}_2$ are the spins. S_z is the z component of the spin, and S^+ and S^- are the spin raising and lowering operators. α is the spin anisotropy, where $\alpha = 1$ is identical with the isotropic case presented in Equation (3-5).

3.2.2 Eigenstates of a magnetic dimer and pseudo-boson operators

Two coupled fermions have an excitation spectrum with boson like properties²⁷.

The eigenstates of a spin $\frac{1}{2}$ dimer are developed, and the pseudo-boson operators that can be used to represent the combined system are presented. The total spin on each atom is $S = \frac{1}{2}$ for the cases considered in this thesis.

The two spin $\frac{1}{2}$ particles can take the state of spin up, or spin down, but the four possible combinations are not all eigenstates of Equation (3–5). The dimer system as a whole has total spin either $S = 0$ or $S = 1$. The eigenstates of the dimer are enumerated in Table 3-1.

There is a gap from the spin 0 ground state to the spin 1 excited state of $E_{\text{gap}} = J$. In the dimer, the spin 1 excited state is three fold degenerate, or a spin 1 triplet, while the ground state is a singlet. The spin 1 triplet could be split by a magnetic field, in order to differentiate the levels.

In the anisotropic dimer model of Equation (3–6), the degeneracy of the triplet is split by the anisotropy. The eigenfunctions of the isotropic and anisotropic dimer systems are identical. In both cases, the degeneracy in the $S = 1$ states can be split using a

Table 3-1 Dimer States and Energies

$ \Psi_{\text{dimer}}\rangle$	S	S_z	E_{Dimer}	$E_{\text{Anisotropic}}$
$ \uparrow\uparrow\rangle$	1	+1	$J/4$	$J/4$
$\frac{1}{\sqrt{2}}(\uparrow\downarrow\rangle + \downarrow\uparrow\rangle)$	1	0	$J/4$	$-J/4 + \alpha J/2$
$ \downarrow\downarrow\rangle$	1	-1	$J/4$	$J/4$
$\frac{1}{\sqrt{2}}(\uparrow\downarrow\rangle - \downarrow\uparrow\rangle)$	0	0	$-3J/4$	$-J/4 - \alpha J/2$

magnetic field (see Table 3-2). It is worth noting that the two modes in the anisotropic dimer system have energies $E = J\alpha$ and $E = \frac{1}{2}(1+\alpha)J$.

Spin-0 and spin-1 states are characteristic of boson particles, and so boson-like creation and annihilation operators can be defined for this system. Taking the spin 0 as the ground state G , the creation operators would then be defined as

$$\begin{aligned} a_0^\dagger |G\rangle &= |0\rangle \\ a_{\bar{1}}^\dagger |G\rangle &= |\bar{1}\rangle \\ a_1^\dagger |G\rangle &= |1\rangle \end{aligned} \tag{3-7}$$

here 0, 1, and $\bar{1}$ are the spin-1 states with $S_z = 0, 1$, and -1 respectively. The Hermitian conjugates of these operators are the annihilation operators, and reduce their respective excited states to the ground state.

Defining the ground state to have energy 0, and knowing the energy gaps of the dimer system from Table 3-1, the Hamiltonians of Equations (3-5) and (3-6), in terms of the boson operators, are

$$\begin{aligned} \hat{H}_{iso} &= J[a_0^\dagger a_0 + a_{\bar{1}}^\dagger a_{\bar{1}} + a_1^\dagger a_1] \\ \hat{H}_{aniso} &= \alpha J a_0^\dagger a_0 + \frac{J(1+\alpha)}{2} [a_{\bar{1}}^\dagger a_{\bar{1}} + a_1^\dagger a_1] \end{aligned} \tag{3-8}$$

These Hamiltonians give the correct energy gaps when operating on any of the eigenstates of the system.²⁸ The operators of Equation (3-8) form the basis of the pseudo-boson approximation.

3.2.3 Dynamic structure factor of a magnetic dimer

The dynamic structure factor for a magnetic dimer can be extracted from the Hamiltonian. The scattering cross section, related by Equation (2-9) to the structure factor, gives the dependence of the scattered intensity on k , from which the dimer spacing

d can be discovered. The dispersion of the dimer can also be calculated, revealing the magnetic dimer to be dispersionless.

The structure factor is given by

$$S(\vec{k}, \omega) = |F(k)|^2 |\langle E' | S_k^z | G \rangle|^2 \delta(\hbar\omega - E') \quad (3-9)$$

provided that the temperature of the system is sufficiently low that few, if any, dimers will be in any but the ground state. The interaction potential V is $F(k)S_k^z$, where $F(k)$ is the form factor of the scattering atom at k , S_k^z is the Fourier transform of S^z for a dimer, G is the ground state of the dimer, and E' is any energy eigenstate of the dimer.

The Fourier transform S_k^z has a simple form for a dimer, since there are only two atoms involved in the system. Specifically,

$$S_k^z = \frac{1}{\sqrt{N}} \sum_i S_i^z e^{-i\vec{k} \cdot \vec{R}_i} = \frac{1}{\sqrt{2}} \left(S_1^z e^{\left(\frac{-i\vec{k} \cdot \vec{d}}{2}\right)} + S_2^z e^{\left(\frac{i\vec{k} \cdot \vec{d}}{2}\right)} \right) \quad (3-10)$$

where d is the dimer separation. The spin operators can be transformed into the pseudo-boson operators by examining the operators effect on the dimer eigenstates. This can be seen by

$$\begin{aligned} S_1^z |G\rangle &= \frac{1}{2} |0\rangle = \frac{1}{2} a_0^\dagger |G\rangle & S_2^z |G\rangle &= -\frac{1}{2} |0\rangle = -\frac{1}{2} a_0^\dagger |G\rangle \\ S_1^z |0\rangle &= \frac{1}{2} |G\rangle = \frac{1}{2} a_0 |0\rangle & S_2^z |0\rangle &= -\frac{1}{2} |G\rangle = -\frac{1}{2} a_0 |0\rangle \\ S_1^z |\bar{1}\rangle &= -\frac{1}{2} |\bar{1}\rangle = \frac{1}{2} a_1^\dagger a_1 |\bar{1}\rangle & S_2^z |\bar{1}\rangle &= -\frac{1}{2} |\bar{1}\rangle = \frac{1}{2} a_1^\dagger a_1 |\bar{1}\rangle \\ S_1^z |1\rangle &= \frac{1}{2} |1\rangle = \frac{1}{2} a_1^\dagger a_1 |1\rangle & S_2^z |1\rangle &= \frac{1}{2} |1\rangle = \frac{1}{2} a_1^\dagger a_1 |1\rangle \end{aligned} \quad (3-11)$$

which allows Equation (3-10) to be rewritten in terms of the pseudo-boson operators, by the simple substitution

$$\begin{aligned}
S_1^z &= \frac{1}{2} (a_0^\dagger + a_0 - a_1^\dagger a_1 + a_1^\dagger a_1) \\
S_2^z &= \frac{1}{2} (-a_0^\dagger - a_0 - a_1^\dagger a_1 + a_1^\dagger a_1)
\end{aligned} \tag{3-12}$$

By using this pseudo-dimer representation of the spin operators in Equations (3-9) and (3-10), the structure factor can be found to be

$$S(\vec{k}, \omega) = |F(k)|^2 \sin^2\left(\frac{\vec{k} \cdot \vec{d}}{2}\right) \delta(\omega - J) \tag{3-13}$$

which shows that the scattered intensity will vary as $\sin^2(\vec{k} \cdot \vec{d} / 2)$, from which the dimer spacing d can be observed. It is also clear that the system is dispersionless. The energy gap does not depend on the momentum transferred to the system.

This result could have been derived directly from the spin operators for the magnetic dimer, without resort to the pseudo-boson operators. The derivation was presented using those operators in order to present them for the more difficult cases of the alternating chain and spin ladder.

3.2.4 Magnetic susceptibility of a magnetic dimer

The magnetic susceptibility of a material is frequently used to examine its magnetic properties. The susceptibility of a material can be calculated in the following manner. For each energy level of a system E_n , the magnetization of the material is

$$M_n(H) = -\frac{dE_n}{dH} \tag{3-14}$$

where H is the applied magnetic field. To examine this, the Hamiltonian of the dimer needs to include the magnetic interaction. The field can be arbitrarily applied in the z direction without any loss of generality. Then, the Hamiltonian for the anisotropic dimer (the isotropic case is identical, but with $\alpha = 1$) becomes

$$\hat{H} = JS_1^z S_2^z + \frac{\alpha J}{2} (S_1^+ S_2^- + S_1^- S_2^+) + g\mu_B H (S_1^z + S_2^z) \quad (3-15)$$

where g is the Landé g -factor and μ_B is the Bohr magneton. The eigenstates of this

Table 3-2 Magnetization of a Dimer

S	S_z	E	M
0	0	$-\frac{J}{4} - \frac{\alpha J}{2}$	0
1	-1	$\frac{J}{4} - g\mu_B H$	$g\mu_B$
1	0	$-\frac{J}{4} + \frac{\alpha J}{2}$	0
1	1	$\frac{J}{4} + g\mu_B H$	$-g\mu_B$

Hamiltonian are the same as for the anisotropic dimer in Table 3-1. The energy levels, however, do change and are listed with the magnetization in Table 3-2.

The sample magnetization at a given temperature is given by

$$M(H, T) = \frac{\sum_n M_n(H) \exp(-\beta E)}{\sum_n \exp(-\beta E)} \quad (3-16)$$

where $\beta = 1/kT$. Then for the anisotropic dimer, the magnetization of the sample is

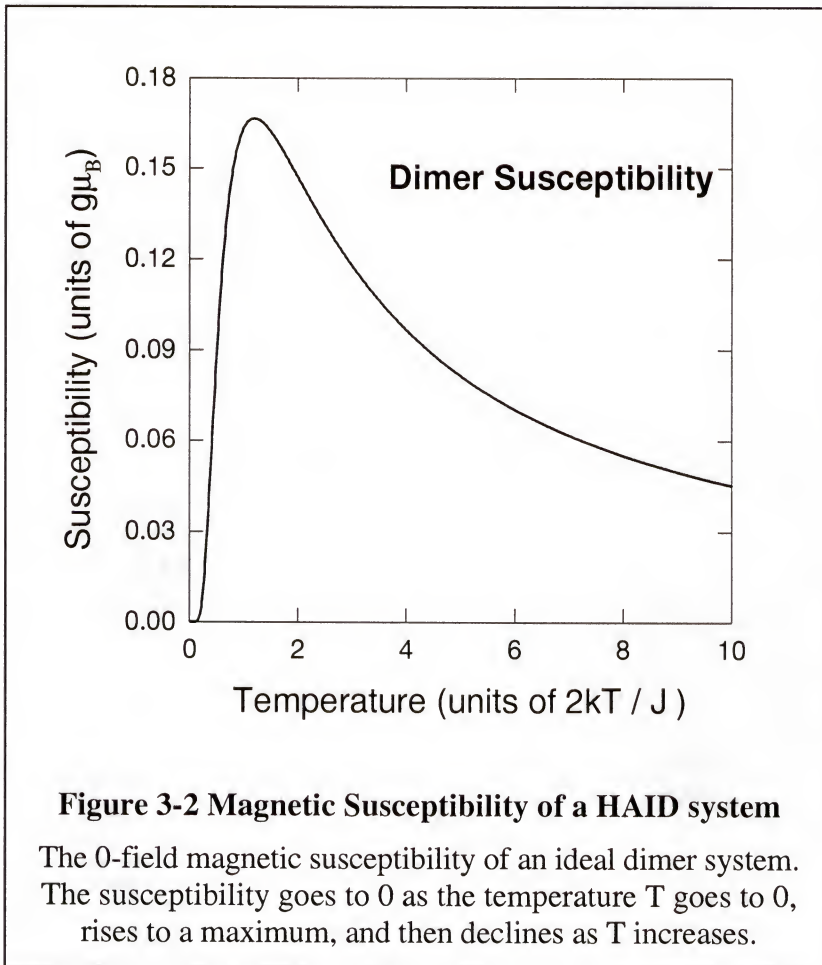
$$M(H, T) = g\mu_B \exp\left(-\frac{\beta J}{4}\right) \left[\frac{\sinh(\beta g\mu_B H)}{\cosh(\beta g\mu_B H) + \exp\left(\frac{\beta J}{2}\right) \cosh\left(\frac{\beta \alpha J}{2}\right)} \right] \quad (3-17)$$

The susceptibility of the sample is therefore

$$\chi(H, T) = \frac{dM}{dH}$$

$$\chi(H, T) = \beta g^2 \mu_B^2 \exp\left(-\frac{\beta J}{4}\right) \left[\frac{1 + \exp\left(\frac{\beta J}{2}\right) \cosh(\beta g \mu_B H) \cosh\left(\frac{\beta \alpha J}{2}\right)}{\left(\cosh(\beta g \mu_B H) + \exp\left(\frac{\beta J}{2}\right) \cosh\left(\frac{\beta \alpha J}{2}\right) \right)^2} \right] \quad (3-18)$$

The 0-field magnetic susceptibility for the isotropic dimer ($\alpha = 1$) versus



temperature is shown in Figure 3-2. The susceptibility goes to 0 as T goes to 0, which is

characteristic of a system with an energy gap. The susceptibility reaches a maximum at the short range order critical temperature, above which the susceptibility follows a Curie-Weiss Law, decreasing to 0 as the temperature goes to infinity.¹⁶

3.3 Dispersion And Susceptibility Of Alternating Chains

An alternating chain is a one-dimensional magnetic system composed of an infinite chain of simple magnetic dimers, each coupled to the following dimer, and is one of the leading explanations for the behavior of $(\text{VO})_2\text{P}_2\text{O}_7$. This section examines the alternating chain, calculating the expected dispersion using the pseudo-boson operators developed in the previous section.

This section begins by describing the alternating chain, developing a Hamiltonian for the isotropic and anisotropic case, and showing examples of real crystals with an alternating chain magnetic structure. The dispersion is then derived from the Hamiltonian using the pseudo-boson operators in section 3.3.2. Finally, the magnetic susceptibility is calculated in section 3.3.3.

3.3.1 Description and Hamiltonian of an alternating chain

The alternating chain is an infinite chain of dimers connected together, but the connection between the dimers does not have to be the same as the connection at the dimer. The system is represented by the Hamiltonian

$$H = \sum_l J_0 \mathbf{S}_1(l) \cdot \mathbf{S}_2(l) + J_1 \mathbf{S}_2(l) \cdot \mathbf{S}_1(l+1) \quad (3-19)$$

where l is the position of a dimer, J_0 is the dimer exchange constant, and $J_1 < J_0$ is the inter-dimer exchange constant. For this to be an antiferromagnetic chain, $J_0, J_1 > 0$. A schematic of an alternating chain is shown in Figure 3-3. The Hamiltonian in Equation

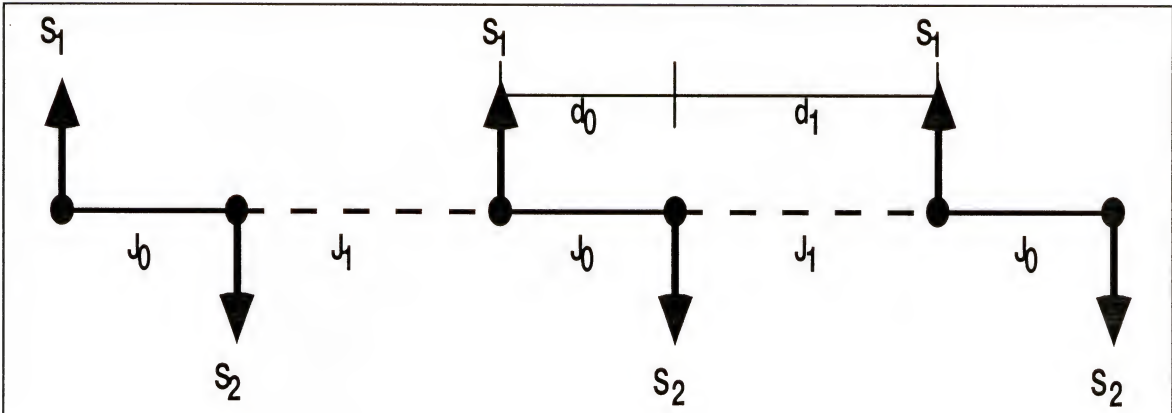


Figure 3-3 Schematic of an Alternating Chain

An alternating chain consists of pairs of spins separated by distance d_0 and interacting with strength J_0 , which are coupled with an identical pair a distance d_1 away with a strength J_1 .

(3–19) describes the Heisenberg antiferromagnetic isotropic alternating chain, or simply the alternating chain for short.

There are limiting cases of the alternating chain. First, the case in which $J_0 = J_1$ is the spin $\frac{1}{2}$ chain, the ground state of which has been solved exactly.²⁵ This is the Heisenberg antiferromagnetic spin chain, or just the spin chain. The other limit is when $J_1 = 0$, which is equivalent to the magnetic dimer considered in the previous section. These two limits can be compared to the results derived for both dispersion and magnetic susceptibility in the remainder of this section.

The Hamiltonian given in equation (3–19) is for the special case of the isotropic alternating chain. The most general case is the Heisenberg antiferromagnetic anisotropic alternating chain, or the anisotropic chain, given by

$$H = \sum_l J_0 \left[S_1^z(l) S_2^z(l) + \frac{\alpha_0}{2} (S_1^+(l) S_2^-(l) + S_1^-(l) S_2^+(l)) \right] + J_1 \left[S_2^z(l) S_1^z(l+1) + \frac{\alpha_1}{2} (S_2^+(l) S_1^-(l+1) + S_2^-(l) S_1^+(l+1)) \right] \quad (3-20)$$

Neither the anisotropic chain nor the isotropic chain have been solved exactly, although a variety of approximation methods have been applied to them.

Antiferromagnetic chains of spins have been observed in real crystals.^{29,30,31} The simplest such system is the Heisenberg chain (equivalent to an alternating chain with $J_0 = J_1$), and it has been observed in multiple systems. Systems with large spins, such as the $S = 5/2$ spin chain, $(\text{CD}_3)_4\text{NMnCl}_3 \cdot 2\text{N}(\text{C}_5\text{D}_5)$, are consistent with classical spin-wave theory.³² The $S = 1/2$ spin chain, in which quantum effects are more important, has been realized in $\text{CuCl}_2 \cdot 2\text{N}(\text{C}_5\text{D}_5)$ ^{33,34} and KCuF_3 ^{35,36}

Alternating chains can also be found. Spin-Peierls materials, for example, become isotropic or anisotropic alternating chains below a transition temperature, as in CuWO_3 ^{2,37} or CuGeO_3 . As another example, the material $(\text{Sr}_{0.8}\text{Ca}_{0.2})_{14}\text{Cu}_{24}\text{O}_{41}$ is claimed to consist of alternating layers of spin ladders (see next section) and alternating chains.³⁸ Other examples of materials that have been claimed to be spin ladders include $\text{Sr}_2\text{Cu}_4\text{O}_6$ ³⁹ and $(\text{VO})_2\text{P}_2\text{O}_7$,⁴⁰ the latter of which will be discussed at length in this thesis.

These examples serve to illustrate that the alternating chain Hamiltonian has a basis in fact. Systems exist that are described by that Hamiltonian, and they are subjects of a considerable body of research.

3.3.2 Dispersion of an alternating chain using pseudo-boson operators

The dispersion of the anisotropic alternating chain has not been solved exactly, but can be approximated using the pseudo-boson operators. The ground state of the $S = 1/2$ spin chain, on the other hand, has been solved exactly²⁵ by what has become known as the Bethe ansatz, and serves as one of the two limits for the alternating chain, the limit in which $J_1 = J_0$. The magnetic dimer of the previous section is the other limit, when $J_1 = 0$. There is no long range order in the spin chain limit of the alternating chain, but the system can be characterized by the dispersion⁴¹

$$\begin{aligned}\omega_L(k) &= \frac{\pi J_0}{2} |\sin(k)| \\ \omega_U(k) &= \pi J \left| \sin\left(\frac{k}{2}\right) \right|\end{aligned}\tag{3-21}$$

where ω_L is the lower limit of the dispersion with a continuum of excitations above it, up to ω_U . This serves as a check on other approximation schemes, as this result is rigorous.

The dispersion of an alternating chain will differ in some important ways from the spin chain dispersion of equation (3-21). Most notably, the effective unit cell doubles when the alternation is introduced, and so the dispersion should vary as $\sin(k/2)$, instead of $\sin(k)$. Also, the spin chain dispersion is gapless, while a gap is predicted for the alternating chain.⁴² The gap should therefore tend to 0 as J_0 approaches J_1 .

In order to apply the pseudo-boson model to the anisotropic chain, one of the exchange paths must be chosen to be the dimer, and the other is a perturbation to it. The stronger exchange, J_0 , is chosen as the basis, so

$$\begin{aligned}H_0 &= J_0 \sum_l \left[S_1^z(l) S_2^z(l) + \frac{\alpha_0}{2} (S_1^+(l) S_2^-(l) + S_1^-(l) S_2^+(l)) \right] \\ H_1 &= J_1 \sum_l \left[S_2^z(l) S_1^z(l+1) + \frac{\alpha_1}{2} (S_2^+(l) S_1^-(l+1) + S_2^-(l) S_1^+(l+1)) \right]\end{aligned}\tag{3-22}$$

While $J_1 < J_0$, there is no requirement that $J_1 \ll J_0$. Applying H_1 as a perturbation appears questionable, but does produce reasonable results.

The rationale for applying H_1 as a perturbation comes from resonating valence bond (RVB) theory. It is not rigorous, but it does provide a physical picture to accompany this approximation.^{42,43} The ground state of an alternating chain (and anisotropic chain) will be antiferromagnetic dimers across the J_0 bond, as shown in Figure 3-4 (a). An excited state that puts some of the bonds across the weaker exchange will leave some spins isolated, as in Figure 3-4 (b). The energy in this state increases linearly with L , and will generally be greater than the excited states of the dimer across the

stronger exchange. It is therefore reasonable to assume the excited states will be localized.

From the Hamiltonian in Equation (3-22), the dispersion can be obtained, and this is detailed in Appendix A. The resulting dispersion is

$$\begin{aligned}\omega_k^L &= \sqrt{\alpha_0 J_0} \sqrt{\alpha_0 J_0 - J_1 \cos(kD)} \\ \omega_k^T &= \sqrt{\frac{J_0(1+\alpha_0)}{2}} \sqrt{\frac{J_0(1+\alpha_0)}{2} - \alpha_1 J_1 \cos(kD)}\end{aligned}\quad (3-23)$$

where ω^L and ω^T are longitudinal and transverse modes of the dispersion, respectively.

This result agrees, to first order, with perturbation theory from the isolated dimer limit.⁴⁴

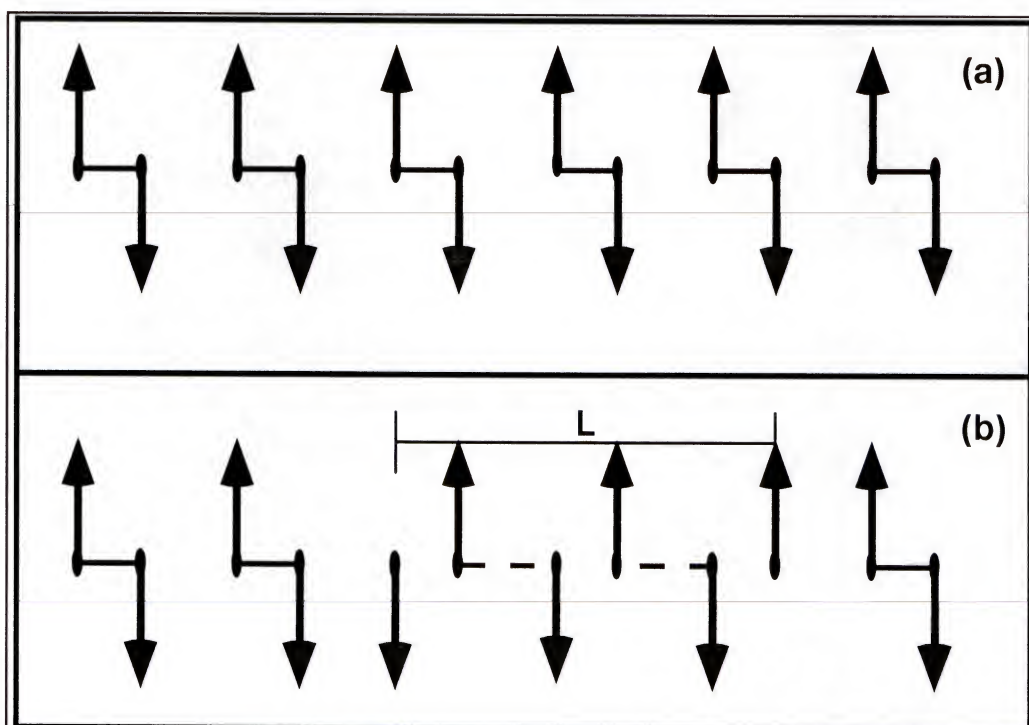


Figure 3-4 Excited Modes in an Alternating Chain

An alternating chain in an excited mode has a single “dimer” pair with spin 1. The lowest energy is gained in the situation in panel (a), in which the coupled spins are neighbors. If the spins are separated, as in panel (b), the energy of the system scales as the distance L between the spins.

The dispersion given in Equation (3–23) behaves properly in the spin chain limit. Taking the anisotropic chain dispersion, with $\alpha_0 = \alpha_1 = 1$, the two modes of the dispersion are exactly equal. As in the dimer case, anisotropy splits the “spin-1 triplet” into two modes. Then, when $J_0 = J_1 = J$, the dispersion reduces to

$$\omega_k = J\sqrt{2} \left| \sin\left(\frac{kD}{2}\right) \right| \quad (3-24)$$

which differs from the correct result of Equation (3–21) by a factor of $\pi(2\sqrt{2})^{-1}$, which is only 11%, and displays the correct shape. Note that the distance $D/2$ would correspond correctly to the spacing between individual spins of Equation(3–21). This approximation only predicts the lower mode, it can not predict the continuum above that mode.

In the dimer limit, where $J_1 = 0$, the dispersion reduces correctly to the dispersionless dimer mode, with $\omega = J_0$. The dispersion behaves properly for the anisotropic dimer limit as well. With $J_1 = 0$, the dispersion shows two energy levels, αJ_0 and $J_0(1+\alpha)/2$.

Both these modes, along with $J_1/J_0 = 0.2, 0.4, 0.6$, and 0.8 , are shown in Figure 3-5.

The dispersion curves in Figure 3-5 also show very clearly that a gap opens immediately when the two exchanges are unequal. The length of the repeating unit D can be determined directly from the dispersion, but it contains no information about the length of the individual exchange paths d_0 or d_1 .

It is also worth noting that, in the case of the anisotropic chain, the transverse and longitudinal dispersion curves can cross, depending on the values of α_0 and α_1 . This is an artifact of the pseudo-dimer approximation, and should be considered a failing in the model if it results.

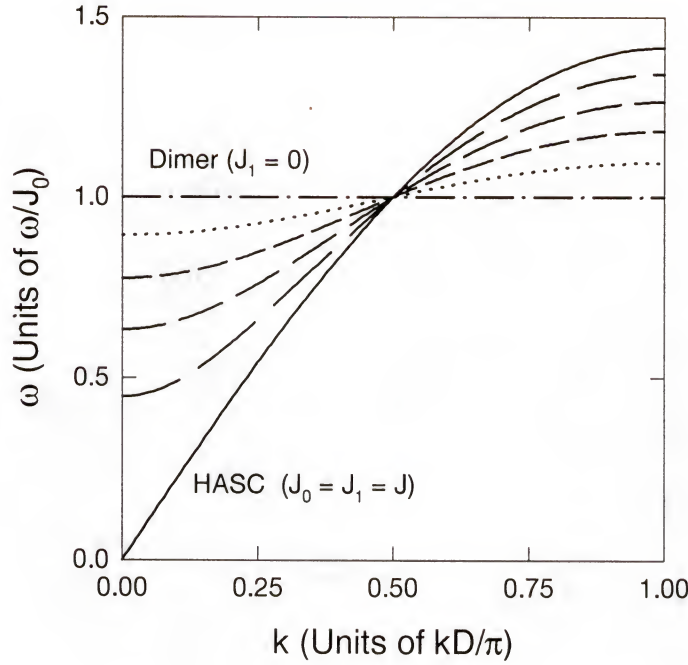


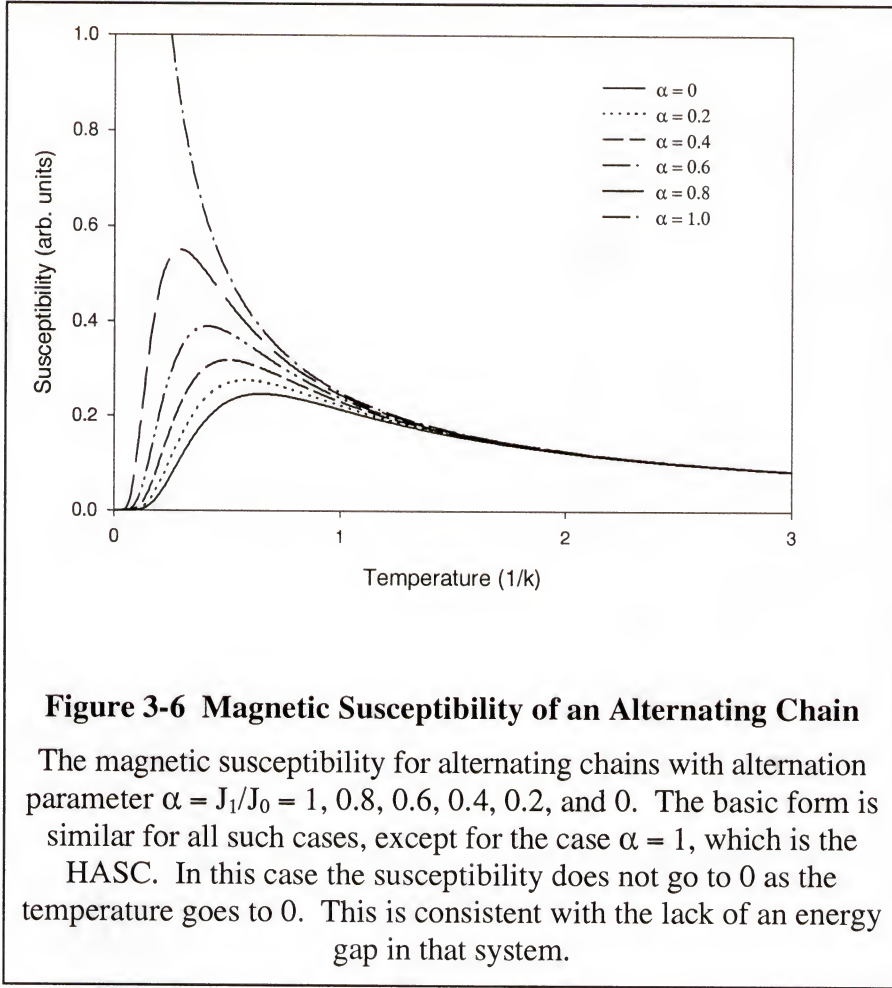
Figure 3-5 Dispersion in an Alternating Chain

The dispersion for alternating chains with an alternation parameter $\alpha = J_1/J_0 = 1, 0.8, 0.6, 0.4, 0.2, 0$ is shown above. The special case $\alpha = 1$ is equivalent to the spin chain, while $\alpha = 0$ is equivalent to a simple dimer. In both these cases the dispersion reduces to the known correct form. An energy gap opens immediately when $\alpha < 1$.

3.3.3 Magnetic susceptibility of an alternating chain

The magnetic susceptibility of an alternating chain is calculated in a similar manner to the dimer. A magnetic term is added to the Hamiltonian

$$H_0 = J_0 \sum_l \left(S_1^z(l) S_2^z(l) + \frac{\alpha_0}{2} (S_1^+(l) S_2^-(l) + S_1^-(l) S_2^+(l)) \right) + g\mu_B H (S_1^z(l) + S_2^z(l)) \quad (3-25)$$



The second term, H_1 is unaltered. This new Hamiltonian is solved in the same manner as the non-magnetic case, and results in a split in the transverse mode,

$$\omega^T = \sqrt{\frac{1}{2} J_0(1 + \alpha_0)} \sqrt{\frac{1}{2} J_0(1 + \alpha_0) - J_1 \alpha_1 \cos(kD)} \pm g \mu_B H \quad (3-26)$$

The longitudinal mode remains unaltered.

The magnetic susceptibility can be calculated in the same manner as in Equation (3-18). The full derivation is shown in Appendix B. The susceptibility is plotted in Figure 3-6, for several values of $\alpha = J_1/J_0$. The case $\alpha = 1$ corresponds to the spin chain, while

the case $\alpha = 0$ corresponds to the anisotropic dimer. All the plots are for the isotropic case, $\alpha_0 = \alpha_1 = 1$.

The case in which $\alpha = J_1/J_0 = 1$, the spin chain limit, is qualitatively different from all other values of α . As the temperature goes to 0, the susceptibility of the spin chain goes to infinity, while all the alternating chains' susceptibility goes to 0. This is due to the lack of an energy gap in the spin chain.

3.4 Dispersion And Susceptibility Of Spin Ladders

To a large extent, spin ladders are the motivating force behind the work done in this thesis. The magnetic systems of the two previous sections were both one dimensional, while a ladder is intermediate between a one and two dimensional system. Considerable theoretical attention has been paid to these systems in recent years,⁴⁵ finding that $S = 1/2$ ladders have an energy gap if they have an even number of chains, but are gapless for odd number of chains.

This section begins by describing the spin ladder, and developing a Hamiltonian for the two-leg antiferromagnetic ladder. Several real systems described by this model are also presented. The dispersion for the two-leg ladder is then calculated using the pseudo-boson operators, and compared to the dispersion calculated by numerical methods for the symmetric spin ladder. Finally, the magnetic susceptibility of the spin ladder is calculated, and compared with the susceptibility of the alternating chain.

3.4.1 Description and Hamiltonian of a spin ladder

A spin ladder consists of two or more spin chains coupled together across “rungs.” This additional coupling changes the character of the interaction from one dimensional to two dimensional. The Hamiltonian for a generalized spin ladder is

$$\hat{H} = J_{\parallel} \sum_{\parallel} S_i \cdot S_j + J_{\perp} \sum_{\perp} S_i \cdot S_j \quad (3-27)$$

where $J_{\parallel}$ is the exchange along the direction of the spin chain, and $J_{\perp}$ is the exchange between the chains. A schematic of the two-leg Heisenberg antiferromagnetic spin ladder (or just the spin ladder for short) is shown in Figure 3-7.

Studies of the spin ladder system have discussed the ground state energy and the dependence of the spin gap on the ratio $J_{\perp} : J_{\parallel}$.⁴⁶⁻⁵⁰ There are several limits that can be considered in discussing the spin ladder system. The first limiting case is $J_{\perp} = 0$, in which case the spin ladder should act as a spin chain. In the alternate limit, when $J_{\parallel} = 0$, the system should act as a set of isolated dimers with separation d_1 . The last case that will be considered is the symmetric case, in which $J_{\perp} = J_{\parallel}$, for which a dispersion has been

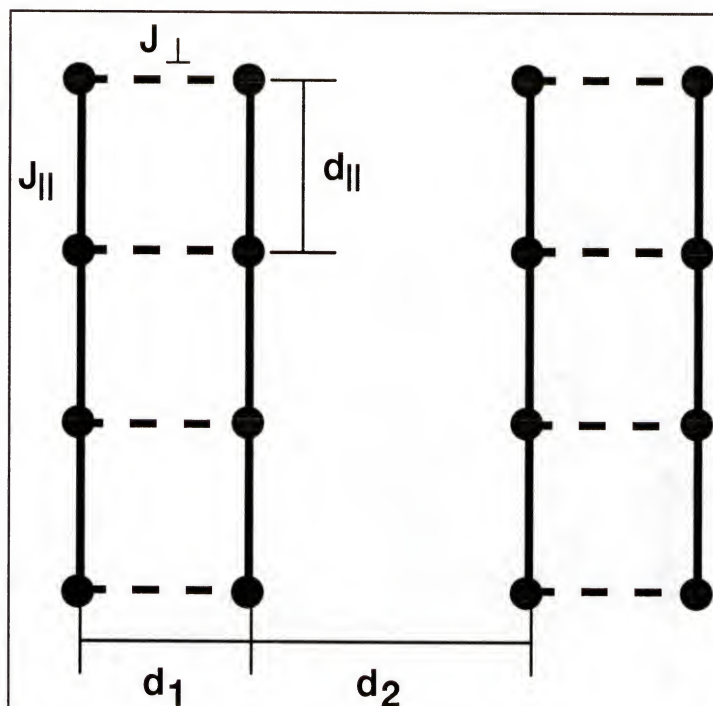


Figure 3-7 Schematic of a Spin Ladder

A spin ladder consists of spins coupled in 2 directions. The “rungs” of the ladder are separated by a distance d_1 , with a distance d_2 to the next ladder. There is no exchange between neighboring ladders.

calculated using Monte Carlo simulations.¹⁰ It has been found that the spin ladder system has an ordered ground state.⁵¹

Finally, as with the dimer and chain models already considered, it is possible to add anisotropy to the spin ladder. In that case, the Hamiltonian becomes

$$\begin{aligned}\hat{H} = & \sum_l J_{\perp} \left(S_1^z(l) S_2^z(l) + \frac{\epsilon_0}{2} (S_1^+(l) S_2^-(l) + S_1^-(l) S_2^+(l)) \right) \\ & + J_{\parallel} \left(S_1^z(l) S_1^z(l+1) + \frac{\epsilon_1}{2} (S_1^+(l) S_1^-(l+1) + S_1^-(l) S_1^+(l+1)) \right) \\ & + J_{\parallel} \left(S_2^z(l) S_2^z(l+1) + \frac{\epsilon_1}{2} (S_2^+(l) S_2^-(l+1) + S_2^-(l) S_2^+(l+1)) \right)\end{aligned}\quad (3-28)$$

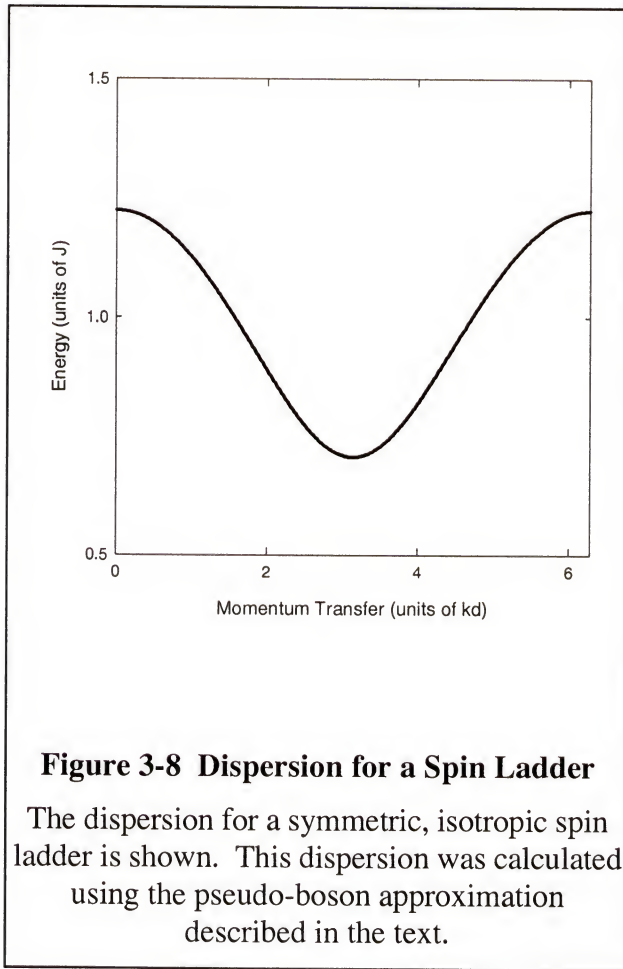
where spins 1 and 2 are a “rung” of the ladder, and the position l is summed along the “length” of the ladder. The rungs and ladders have different anisotropy, ϵ_0 and ϵ_1 .

Spin ladders have been observed in several real compounds.^{52,53} Examples of 2-leg, 3-leg, and more, ladders have been observed in a Sr-Cu-O series⁵⁴, and a La-Cu-O series⁵⁵. Another 2-leg spin ladder has been observed in $\text{Cu}_2(\text{C}_5\text{H}_{12}\text{N}_2)_2\text{Cl}_4$.⁵⁶ Superconductivity has been reported in the Sr-Cu-O series under Ca doping.

Additionally, $(\text{VO})_2\text{P}_2\text{O}_7$ has been reported as the prototypical spin ladder system⁴⁰. The magnetic properties of this material are studied in depth in this thesis.

3.4.2 Dispersion of a spin ladder using pseudo-boson operators

Unlike the alternating chain model considered earlier in this chapter, it is not possible to simply choose the stronger of the two interactions as the basis for perturbation theory. The system can be pictured as a series of coupled dimers if $J_{\perp} > J_{\parallel}$, using reasoning similar to that applied for the alternating chain model. However, this approximation can be expected to fail if $J_{\perp} < J_{\parallel}$. In that case, it is reasonable to begin with the spin chain, and place a coupling between them as a perturbation. This case has been considered using spin wave theory⁵⁷ and Monte Carlo simulations⁵⁸.

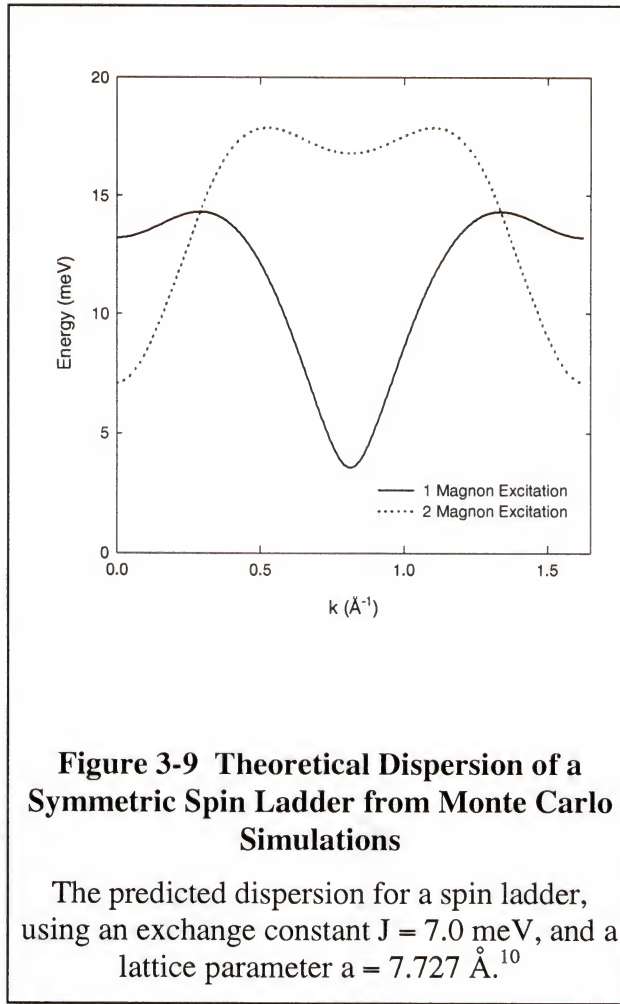


However, the same pseudo-dimer approximation used successfully on the alternating chain also works well on the spin ladder, even up to the symmetric case, although it can be expected to fail when $J_{\perp} < J_{\parallel}$. That is the approach taken in Appendix A. The resulting dispersion is

$$\omega_k^L = \sqrt{\epsilon_0 J_{\perp}} \sqrt{\epsilon_0 J_{\perp} + \frac{J_{\parallel}}{2} \cos(kd_{\perp})}$$

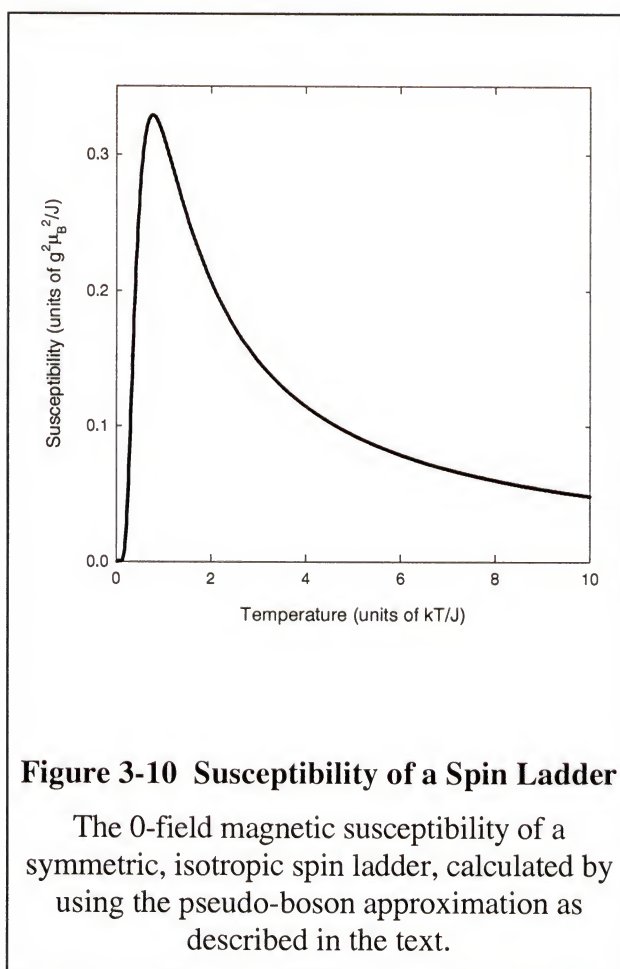
$$\omega_k^T = \sqrt{\frac{J_{\perp}(1+\epsilon_0)}{2}} \sqrt{\frac{J_{\perp}(1+\epsilon_0)}{2} + \frac{J_{\parallel}}{2} \epsilon_1 \cos(kd_{\perp})} \quad (3-29)$$

The dispersion for the spin ladder is shown in (3-29). It is worth looking at the limiting cases. When $J_{\parallel} = 0$, the isotropic case reduces immediately to $\omega = J$. The



anisotropic cases also correspond exactly. On the other hand, in the spin chain limit, where $J_{\perp} = 0$, the dispersion becomes $\omega = 0$. As expected, the pseudo-dimer approximation fails in the spin chain limit.

The symmetric case is the more interesting case. The dispersion for the isotropic, symmetric spin ladder is shown in Figure 3-8. An energy gap is evident, with a minimum at $kd_{\perp} = \pi$. Another calculation of the symmetric spin ladder was performed in Ref. 10 using Monte Carlo simulations of 12-22 rung spin ladders,^{59,60} and is shown in Figure 3-9. The lower mode of that calculation compares favorably with that calculated by the pseudo-boson method.



The dispersions calculated for the symmetric spin ladder by the pseudo-boson model (Figure 3-8) and Monte Carlo simulation (Figure 3-9) compare favorably except at the zone boundaries. Most notably, for the same exchange strength J , both models give the same energy gap. The pseudo-boson model fails to predict the two-magnon mode at all.

3.4.3 Magnetic susceptibility of a spin ladder

The magnetic susceptibility is calculated as in Equation (3–25) for the alternating chain. The full calculation is shown in Appendix B. The magnetic term added to the Hamiltonian splits the transverse mode, leading to a new dispersion relation

$$\omega^T = \sqrt{\frac{J_{\perp}(1+\varepsilon_0)}{2}} \sqrt{\frac{J_{\perp}(1+\varepsilon_0)}{2} + \frac{J_{\parallel}\varepsilon_1}{2} \cos(kd_{\perp})} \pm g\mu_B H \quad (3-30)$$

while the longitudinal mode is unaltered.

The susceptibility is plotted in Figure 3-10, for the symmetric isotropic case.

Comparing this to the alternating chain susceptibility in Figure 3-6 reveals that the two

cannot be distinguished, a fact that has been noted in previous work.⁶¹ In fact, the

thermodynamics of spin- $1/2$ alternating chains and ladders are virtually indistinguishable.^{62,63}

CHAPTER 4

NEUTRON SCATTERING MEASUREMENTS OF DIMER EXCITATIONS IN A POWDER OF $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$

Vanadyl hydrogen phosphate hemihydrate, $\text{VO}(\text{HPO}_4) \cdot \frac{1}{2}\text{H}_2\text{O}$ (or $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$ when deuterated, abbreviated as VODPO), is the precursor to the proposed spin ladder system vanadyl pyrophosphate. This system is known to be a magnetic dimer, and its structure is sufficiently similar to $(\text{VO})_2\text{P}_2\text{O}_7$ (or VOPO) to provide some insight into the magnetic properties of VOPO. It was studied in this thesis primarily for that reason.

The chapter begins with a discussion of the known properties of VODPO. Its structure and magnetic properties are discussed. Section 4.2 discusses a neutron diffraction experiment on a powder sample of VODPO. The method by which the sample of VODPO was grown is discussed, the results of the diffraction experiment are shown, and the refinements to the structural parameters presented in the section 4.1 are detailed. Section 4.3 discusses an inelastic neutron experiment performed on the sample. The dispersion is measured, and shown to be consistent with a magnetic dimer. In the final section, 4.4, the dimer separation distance is calculated, and a path for the magnetic exchange is presented.

4.1 Structure And Magnetic Exchange In $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$

Much of the work done previously on VODPO has been motivated by an interest in VOPO. As such, much research has been done on the nature of the transformation from VODPO to VOPO.^{64,65} It is known from that work that VODPO undergoes a topotactic transformation at 400°C.^{66,67} Single crystals of VODPO become pseudomorphs of VOPO,⁶⁸ with cracks and voids introduced by the distortion of the lattice constants.

The nature of this transformation makes it unsuitable for development of single crystals of VOPO, but its ease makes it ideal for producing powders.⁶⁹⁻⁷²

The crystal structure of VODPO has been thoroughly investigated in the course of investigating its transformation to VOPO. The unit cell is orthorhombic, with space group Pmmn, and lattice constants $a = 7.42 \text{ \AA}$, $b = 9.59 \text{ \AA}$, and $c = 5.69 \text{ \AA}$.⁶⁴ The atomic positions determined by the analysis contained in this thesis are found in Table 4-3.

The magnetic properties of VODPO have also been investigated.^{73,74} It is known to be a magnetic dimer, with $J = 3.70 \text{ meV}$.⁷⁵ The dimer spacing has been assumed to be $3.1 \text{ \AA}$,⁷⁶ the distance between nearest neighbor vanadium ions, and this assumption has been backed up with chemical bonding arguments.⁹ The magnetic properties have been studied through magnetic susceptibility,⁷⁷⁻⁸⁰ electron-phonon resonance, and nuclear magnetic resonance. Neutron scattering experiments have not previously been done on this system.

A summary of the known properties of VODPO is contained in Table 4-1.

Table 4-1 Properties of VODPO

Space Group	Pmmn
a (lattice constant)	$7.416 \text{ \AA}$
b (lattice constant)	$9.592 \text{ \AA}$
c (lattice constant)	$5.689 \text{ \AA}$
Magnetic Exchange	Dimer
J (exchange energy)	7.40 meV
d (inter-dimer spacing)	$3.094 \text{ \AA}$

4.2 Neutron Diffraction Experiment On $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$ Powder

A sample of VODPO was grown, using deuterium in place of hydrogen in order to aid neutron scattering. Neutron diffraction experiments were used in order to verify that the sample was VODPO, was free of contamination, and had successfully replaced hydrogen with deuterium. This section begins by discussing the methods used to grow the sample of VODPO, then presents the results of the neutron diffraction experiment, and concludes with an examination of the structure of VODPO determined in the experiment.

4.2.1 Growth and preparation of $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$ powder

In order to aid neutron scattering, deuterium was used in place of hydrogen in a powder sample of VODPO. The sample was synthesized by refluxing 12 g of V_2O_5 , 60 ml of 85 wt. % D_3PO_4 in D_2O and 230 ml of D_2O under nitrogen for 2 days. The product of this reaction was collected by filtration in a nitrogen glove bag, analyzed with x-ray powder diffraction, and found to be $\text{VOPO} \cdot 2\text{D}_2\text{O}$. This, in turn, was washed with isopropanol- d_8 , transferred to a teflon-lined reaction vessel, and heated with 150 g isopropanol- d_8 under autogenous pressure at 125°C for 7 days. The product was isolated by filtering and drying in a nitrogen glove bag.

This product was then analyzed using x-ray powder diffraction, and was found to be consistent with $\text{VO}(\text{HPO}_4) \cdot \frac{1}{2}\text{H}_2\text{O}$. Additional analyses were performed to verify this, and to determine the fraction of deuterium in the sample. Chemical analyses confirmed that the ratio of P/V was 1.00. Infrared spectroscopy showed a ratio of H/D of 0.04. This was sufficiently pure to consider the sample VODPO.¹⁴

4.2.2 Neutron diffraction of a powder of $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$

The neutron diffraction experiment was performed at the HB4 spectrometer at Oak Ridge National Laboratory (see Figure 2-2). A resulting powder pattern is displayed, and discussed in terms of the results of a Rietveld analysis.

For this experiment, a powder sample consisting of 17g of powdered material was placed in an aluminum cylinder, and cooled in a closed cycle refrigerator. The temperature could be controlled from 10K to 300K with an accuracy of $\pm 0.1\text{K}$. An aluminum cylinder is not ideal for powder diffraction experiments, as the aluminum also has a structure that must be considered when analyzing the data, and the container is not a powder, but a collection of oriented crystallites. This container was used despite these problems in order to use the same sample in later inelastic scattering experiments, for which an aluminum cylinder is far better suited. The HB4 spectrometer used a collimation pre-monochromator - pre-sample - post-sample of 60° - 60° - 6° .

Powder patterns for the VODPO sample were obtained at 10K and 300K. There were no appreciable differences between the two, confirming the lack of a structural phase transition at low temperatures. The powder pattern obtained at 10K is shown in Figure 4-1, along with the fit described in the following section. The lines beneath the graph correspond to the expected peak positions of VODPO (bottom lines) and Al (top lines).

The peaks that are poorly fit to the data correspond to the location of expected aluminum peaks, as shown by the top set of lines. Since the aluminum container is not a powder, it is expected that the fit obtained by the Rietveld analysis would fail for it. This is not a matter for concern however, since the properties of the aluminum are not under investigation. In the remainder of this chapter, only the VODPO data will be discussed. The error in the VODPO data due to the aluminum container is estimated at less than 0.7% by the Rietveld analysis.

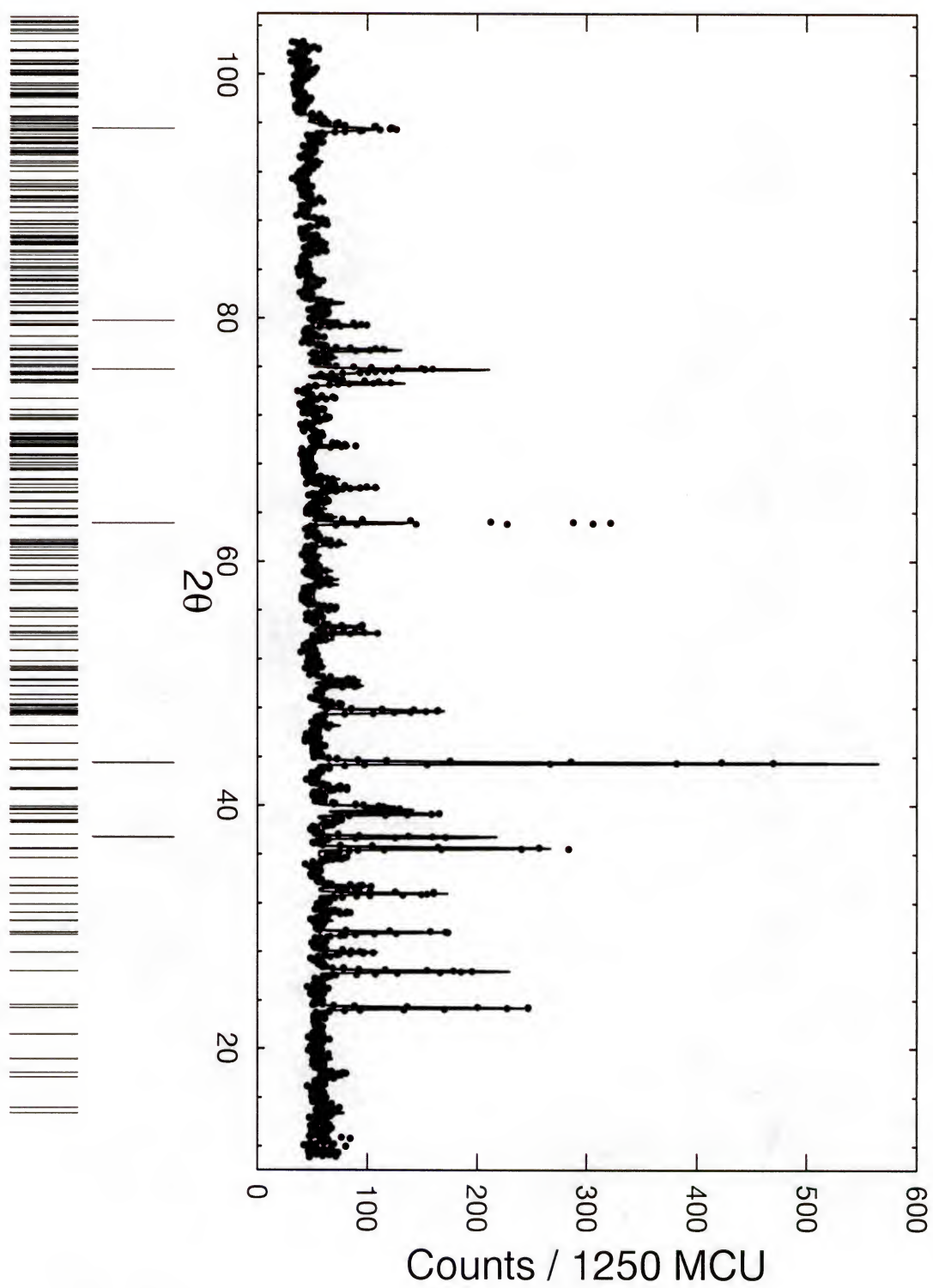


Figure 4-1 VODPO Powder Pattern at 10K

4.2.3 Structure of $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$ determined by Rietvelt analysis

Rietvelt analysis is a method used to determine the structure of a material from a powder pattern. Progressive least squares refinements are performed to determine the structure's space group, lattice constants, atomic positions, and atomic thermal ellipsoid radii. Additionally, if one lattice position can be occupied by two types of atoms, as with H and D in VODPO, this method can be used to determine the fractional amount of each type at each site.

In accord with previous results,⁶⁴ VODPO was found to have a space group of Pmmn, which is an orthorhombic structure with 8 equivalent sites for each atom in the unit cell. The lattice parameters remained stable, shrinking by a maximum of 0.18% when

Table 4-2 VODPO Lattice Constants

	a (Å)	b (Å)	c (Å)
10K	7.4102 (6)	9.5860 (8)	5.6874 (6)
300K	7.4228 (5)	9.6037 (8)	5.6969 (6)

cooling from 300K to 10K. The lattice parameters at each temperature are summarized in Table 4-2.

The atom positions were also refined by this process, and are summarized in Table 4-3. The positions quoted are in fractional units of the lattice parameter, where x corresponds to the a direction, y to b, and z to c. The vanadium position was not refined by this process. Due to the extremely low scattering length of vanadium, its position could not be refined by the data collected. Instead, the position obtained by x-ray scattering in ref. 64 was retained.

Table 4-3 Atomic Positions in VODPO

Atom	x - 10K	y - 10K	z - 10K	x - 300K	y - 300K	z - 300K
V	0.0418 (0)	0.250 (0)	0.0308 (0)	0.0418 (0)	0.250 (0)	0.0308 (0)
P	0.250 (0)	0.539 (2)	0.175 (9)	0.250 (0)	0.532 (2)	0.218 (5)
O	0.250 (0)	0.504 (2)	0.424 (5)	0.250 (0)	0.509 (3)	0.480 (5)
O	0.0808 (15)	0.609 (1)	0.132 (2)	0.0775 (15)	0.609 (2)	0.151 (3)
O	0.250 (0)	0.382 (4)	0.114 (9)	0.250 (0)	0.385 (2)	0.100 (4)
O	0.939 (3)	0.250 (0)	0.305 (4)	0.941 (3)	0.250 (0)	0.282 (5)
O	0.250 (0)	0.250 (0)	0.818 (6)	0.250 (0)	0.250 (0)	0.753 (7)
D	0.250 (0)	0.532 (5)	0.599 (10)	0.250 (0)	0.566 (5)	0.597 (10)
D	0.250 (0)	0.187 (2)	0.635 (4)	0.250 (0)	0.178 (2)	0.616 (5)

Symmetry positions are not refined in a Rietvelt analysis. In VODPO, the symmetry positions are at (0.25 k l), (h 0.25 l), and (h k 0), or combinations thereof.

The ratio of H/D was allowed to vary independently at its two sites. At one site, the fraction of hydrogen was 2.7(4.2)%, at the other it was 12.3(8.6)%. The small scattering length of hydrogen leads to the large errors in those values. These results are consistent with the 4% H/D value found by infrared spectroscopy.¹⁴

The structure of the VODPO molecule is shown in Figure 4-2. Part (a) shows the unit cell, with the VO₆ octahedra, joined along an edge, separated from the next VO₆ octahedra pair by PO₄ tetrahedra. These chains are separated in the c direction by D atoms, the hydrated water molecules. Section (b) shows a schematic representation of the projection of the structure into the a-b plane. Two possible magnetic exchange paths are illustrated. The path P1 represents the shorter distance between two V⁴⁺ ions, through the

edge joined octahedra, with a length of $3.09\text{\AA}$, while P2 represent the path through a PO_4 tetrahedra, with a length of $4.20\text{\AA}$.

4.3 Inelastic Neutron Scattering Experiment On $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$ Powder

Inelastic neutron scattering on the sample of VODPO had two main purposes. First, it would establish whether or not VODPO was simply a dimer, as previously indicated by magnetic susceptibility. Secondly, if it was a dimer, the distance between magnetic ions in the dimer could be determined. This, in turn, was important because the dimer in VODPO was believed to be the same as the ‘rung’ in the spin ladder model of VOPO (see Chapter 5 for more discussion of VOPO).

Section 4.3.1 begins with a discussion of the experimental setup used for the experiments. The temperature dependence of the neutron scattering is then discussed in Section 4.3.2, followed by a series of inelastic neutron scattering scans at constant-Q and constant-E, all at low temperature, in Section 4.3.3. The determination of the dimer separation distance concludes this Section in 4.3.4.

4.3.1 Inelastic neutron scattering experiment setup parameters

The same sample used to obtain the structure data was used in this experiment. The aluminum can containing the sample is ideal for inelastic neutron scattering experiments. Aluminum has a very low absorption cross section, allowing a maximum number of neutrons to pass. This is important in inelastic experiments, where the scattering cross section is frequently low.

The sample was cooled in a closed cycle refrigerator, in which the temperature could be controlled from 10K to 300K, with an accuracy of $\pm 0.1\text{K}$. A temperature of 10K was used as the base in this experiment.

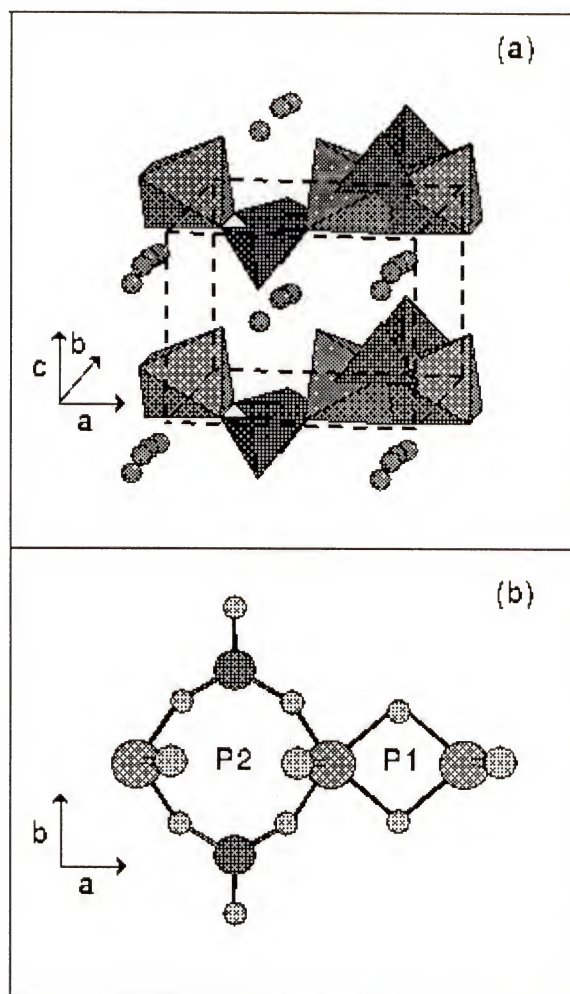


Figure 4-2 Structure of VODPO

The structure of VODPO is illustrated. Panel (a) shows a unit cell, with edge-sharing VO_6 octahedra separated by PO_4 tetrahedra. Isolated D atoms (shown as spheres) separate layers in the c direction. Panel (b) shows a projection of the structure in the a - b plane. Path P1 illustrates the nearest neighbor V-O-V path, while P2 is the V-O-P-O-V path through a phosphate tetrahedra

VODPO was expected to be a dimer, and thus to have no dispersion. Resolution calculations⁸¹ showed that opening the beam gave great increases of intensity with little loss of resolution. A horizontally curved analyzer was used to increase this effect, and gain even greater intensity. Two experimental setups are shown in Table 4-4, along with

Table 4-4 HB1 Spectrometer Configuration

Pre-Mono.	Pre-Sample	Post-Sample	Post-Anal.	Phonon Width (meV* Å ⁻¹)	Intensity (arb. units)
40'	40'	60'	60'	0.344	0.153
40'	40'	240'	240'	0.375	1.44

the resolution parameters resulting from them. Both setups use the horizontally curved analyzer.

The phonon width in Table 4-4 is a simple measure of the resolution of the setup. The smaller the value, the better the resolution. The intensity is a scale measure of the flux incident on the sample. For the sample resolutions shown, the second, looser configuration gives nearly ten times the flux, for a loss of resolution of only 9.0%. The second set of collimations was the one used for this experiment.

For these experiments, a constant final energy, $E_f = 13.5$ meV, was used. Two types of typical inelastic scattering experiment scans were used in these experiments; scans of constant momentum transfer Q (constant- Q scans), and scans of constant energy transfer E (constant- E scans).

4.3.2 Inelastic neutron scattering intensity variation with temperature

The temperature dependence of an inelastic neutron scattering peak can be used to determine the nature of the interaction. A magnetic peak keeps the same total intensity⁸², but the width of the peak increases with temperature, thus decreasing the peak height considerably. A phonon increases its total intensity at higher temperature, thus increasing its peak height.⁸³

A constant-Q scan at $Q=1.0 \text{ \AA}^{-1}$ quickly revealed a peak at 7.86 meV. This was consistent with the dimer energy of 7.40 meV reported in magnetic susceptibility studies.¹⁰ Additional evidence that this peak comes from the magnetic spin coupling and not, for example, from a phonon, can be obtained by examining the temperature dependence of the peak. Four scans at the same constant-Q are shown at varying temperatures in Figure 4-3.

The peaks in Figure 4-3 are separated by adding a constant background to the different scans. A gaussian with a linear background, of the form

$$I = A \exp\left(-\frac{(E - E_c)^2}{2\sigma^2}\right) + A_1 E + A_2 \quad (4-1)$$

was then fit to the data, where A is the peak intensity, E_c is the peak center, σ is the half-width, and A_1 and A_2 are the linear and constant backgrounds. A constant background, A_2 in this example, is common in scattering experiments due to fast neutrons, background radiation, and incoherent neutron scattering from the sample. The linear background A_1 is most likely due to a phonon beyond the observed range. It is not strong in the results in this figure, but is necessary at other constant-Q scans, and is included in order to use the same fit on all the data. The decreasing goodness-of-fit, most obvious on the 200K scan, is simply due to decreasing intensity, and increasing fluctuations.

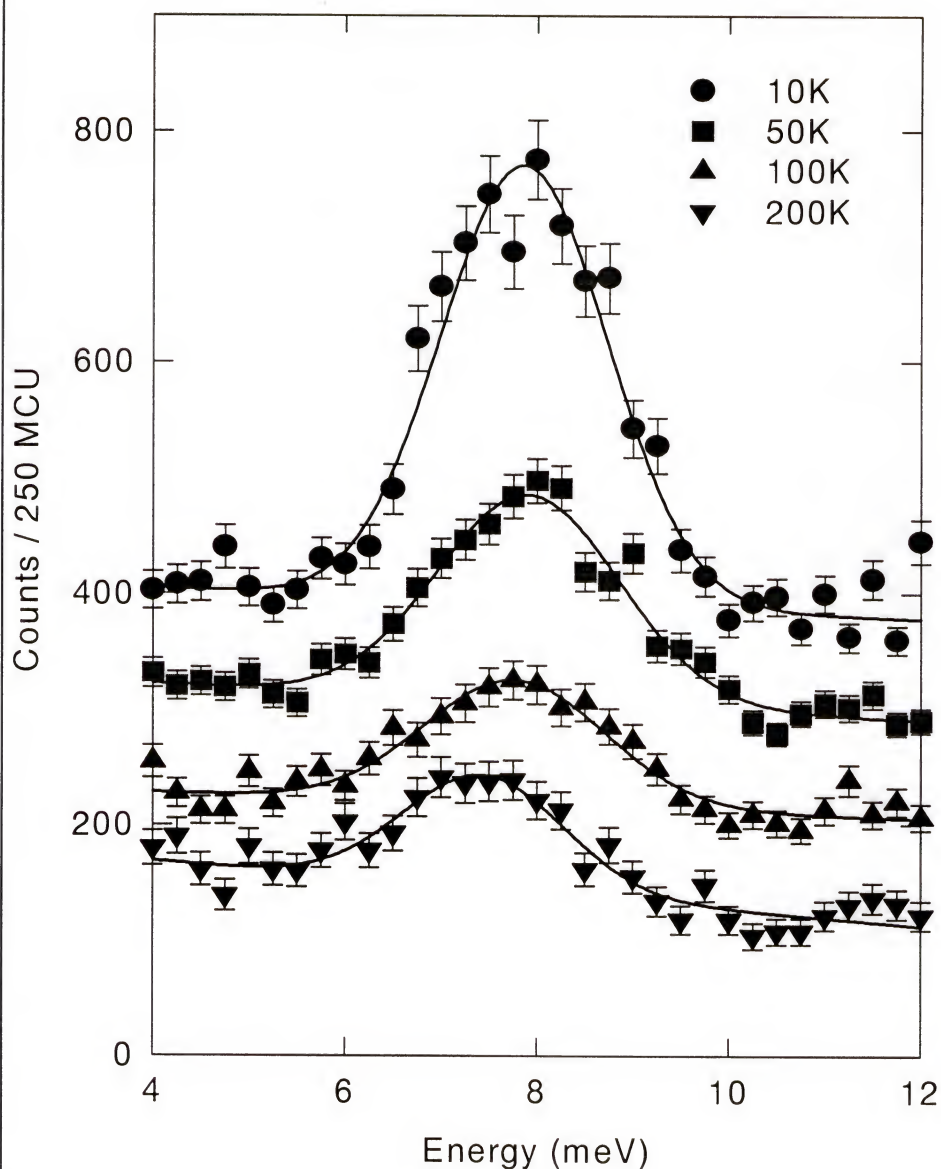


Figure 4-3 Temperature Dependence of VODPO Inelastic Peak

The peak observed in VODPO at 7.86 meV is shown at temperatures from $T=10\text{K}$ to $T=200\text{K}$. Each scan is a constant-Q scan taken at $1.0 \text{ \AA}^{-1}$. A constant background of 50 is added to successive scans for clarity of presentation. It is easily observed that the maximum intensity decreases as temperature increases, consistent with a magnetic origin for the peak.

The fitted parameters are displayed in Table 4-5. They show all the parameters from equation (4-1), plus the total intensity of the gaussian peak. The constant background A_2 is shown for the original scan, without the extra addition used in Figure 4-3 to separate the curves. The decrease in amplitude A with temperature provides evidence

Table 4-5 Parameters for Temperature Dependence

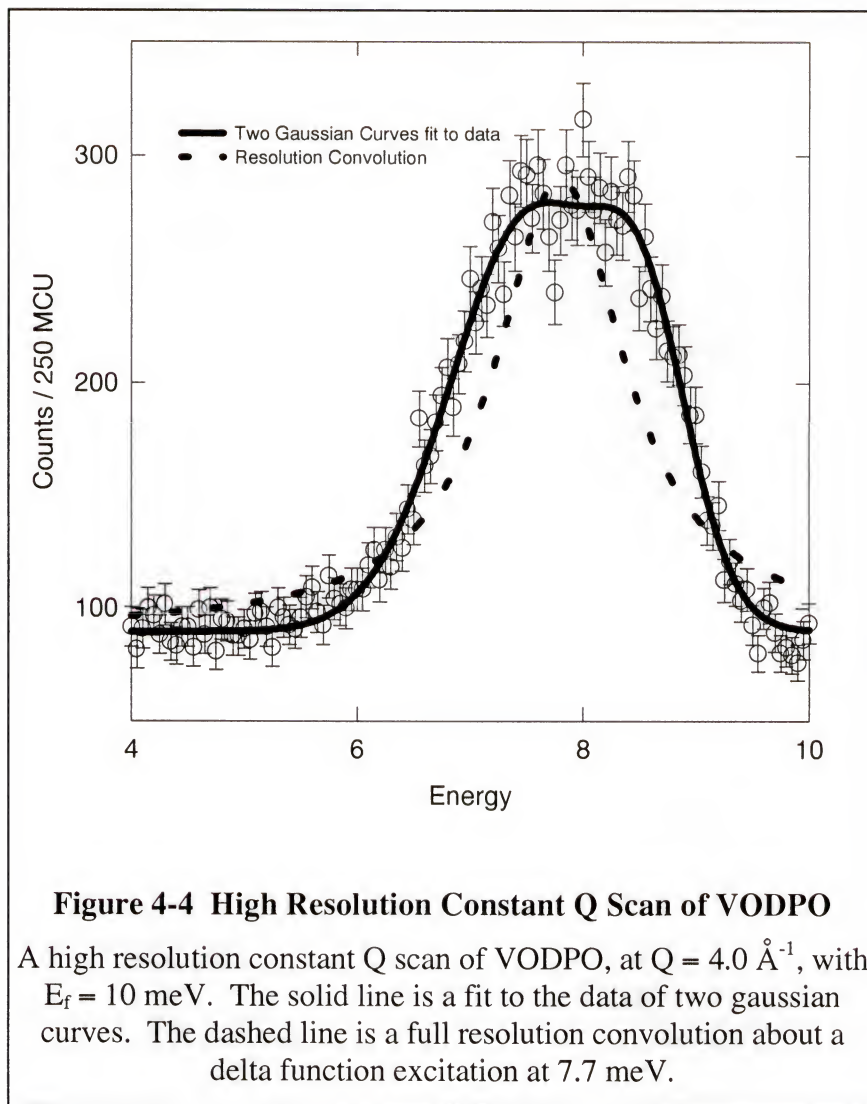
T (K)	A (meV)	E_c (meV)	σ (meV)	A_1 (meV*Å)	A_2 (meV)	Intensity(meV)
10	377.8 (213)	7.86 (5)	0.868 (48)	-3.38 (170)	118 (16)	770. (54)
50	178.5 (93)	7.91 (5)	0.952 (57)	-3.99 (101)	138 (9)	332 (26)
100	107.5 (79)	7.76 (8)	0.946 (84)	-3.00 (99)	141 (9)	202 (21)
200	98.7 (97)	7.44 (9)	0.836 (97)	-7.13 (120)	198 (12)	353 (54)

that this is a magnetic peak. The integrated intensity of the peak decreases from its maximum value at 10K as the temperature increases.

The widths of the curve in Figure 4-3 are limited by the resolution, but the resolution was increased by lowering the final energy to 10 meV, and the resulting scan at 4.0 Å^{-1} is shown in Figure 4-4. The dashed line is resolution convolution about a delta function peak for a dispersionless dimer. This fit is narrower than the observed data, indicating either some small anisotropy or dispersion due to additional interactions. The maximum anisotropy consistent with the observed data is 1.2.

4.3.3 Dispersion of $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$ at 10K

The dispersion of the VODPO powder is determined by examining a series of constant-Q scans, taken at $T=10\text{K}$. The same energy range was examined at 0.1 Å^{-1} steps



from $Q = 1.0 \text{ \AA}^{-1}$ to $Q = 4.5 \text{ \AA}^{-1}$. Each scan was fit as in equation (4-1). The results of that fit for A_1 , A_2 , E_c and σ are shown in Figure 4-5.

The parameter fits give considerable information. In Figure 4-5(a), the peak center E_c is nearly constant, so the fit is effectively dispersionless. This is consistent with a simple dimer, as shown in equation (3-13), and confirms the results of magnetic susceptibility studies. There is a small, 3.6%, drop in the peak center at high- Q . This is likely caused by a combination of increasing error due to falling intensity, and a real effect of small next-nearest neighbor coupling in the material. The half-width, shown in Figure 4-

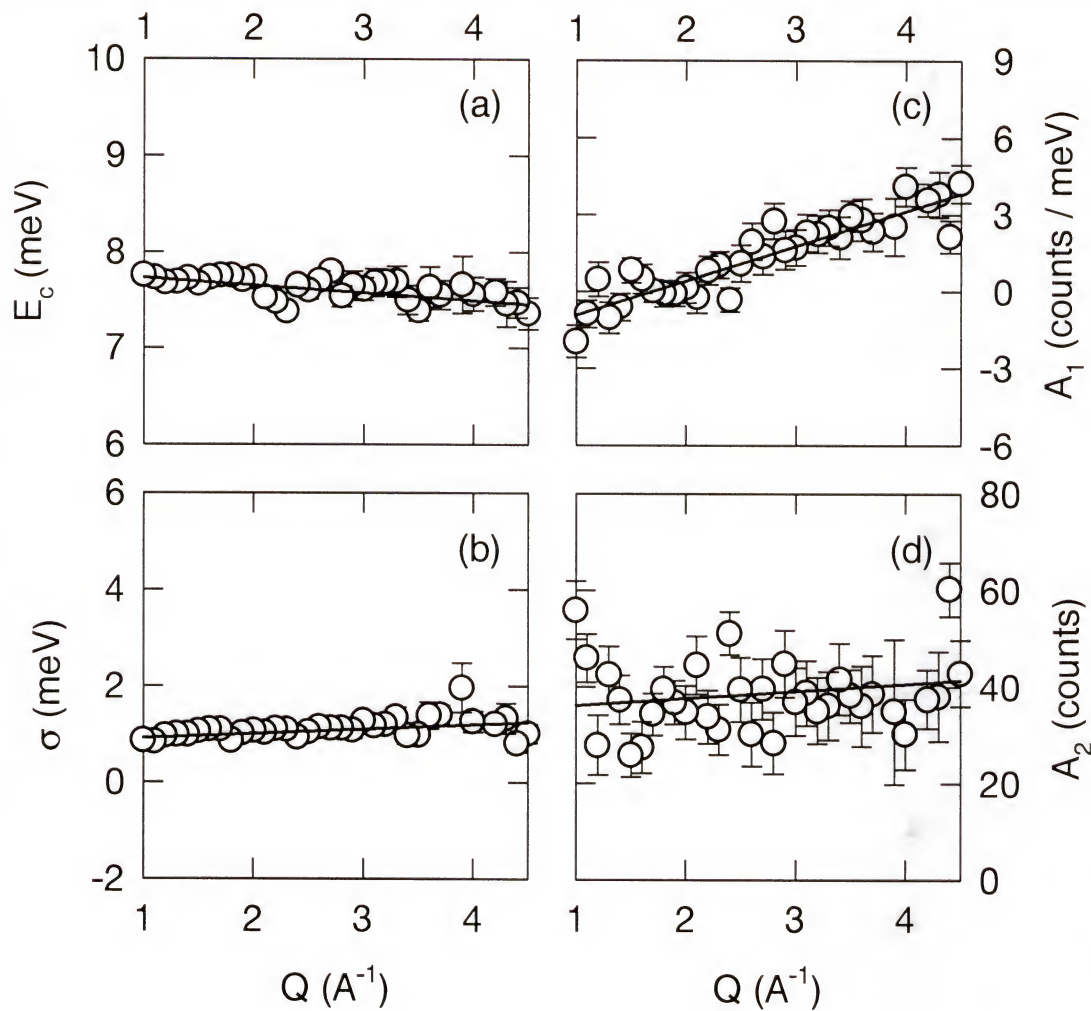


Figure 4-5 Parameters for Constant-Q Scans

Results of the fits of Equation (4-1) to the constant-Q scans of a powder sample of VODPO. Panel (a) shows the energy E of the excitations, panel (b) shows the half-width σ of the excitation, and panels (c) and (d) show the linear and constant portions of the background respectively. The constant-Q scans used in the fits are separated by $0.1 \text{ \AA}^{-1}$ intervals. Each scan was taken at 10K, with a fixed final neutron energy of 13.5 meV.

5(b), increases slightly with Q . Some of this increase is a resolution effect due to the horizontally focusing analyzer, but the magnitude of the increase is greater than can be accounted for with resolution effects alone. The increase is likely due to deviations from the simple-dimer model, to be expected in real systems.

The backgrounds behave in an expected manner. The linear background A_1 in Figure 4-5(c) increases with Q , while the constant background A_2 in Figure 4-5(d) is nearly constant throughout the range of Q . An increase in peak intensity with Q is

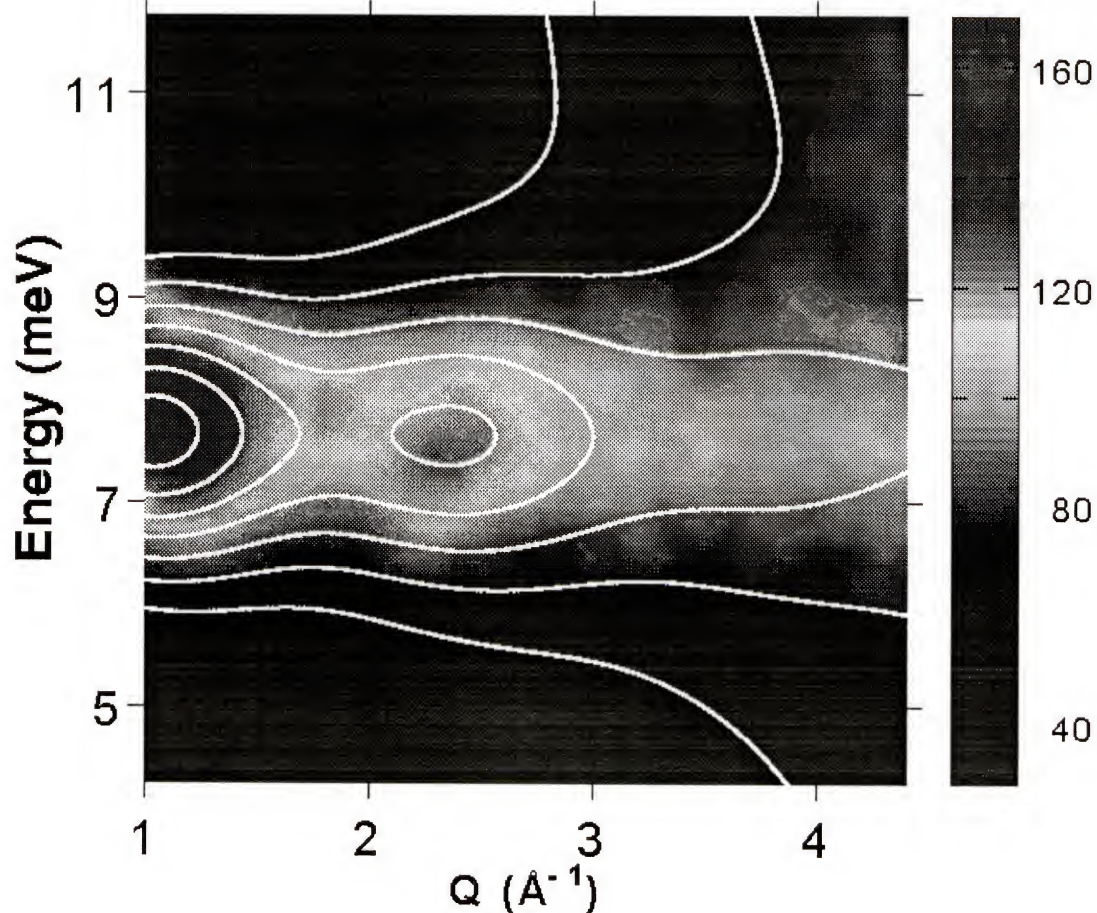


Figure 4-6 2-D Intensity Map of VODPO Peaks

A two dimensional plot of the intensity from a series of constant- Q scans on a powder sample of VODPO. All scans were taken at 10K, with a constant final energy of 13.5 meV on the HB3 spectrometer at ORNL.

consistent with a phonon peak occurring beyond the observed energy range.

The data from all constant-Q scans are combined and displayed in Figure 4-6. The two-dimensional gray scale map displays the intensity at all points. The fits shown by the solid white lines is described in Section 4.3.4.

4.3.4 Dimer separation in $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$

The intensity expected for a dimer system is given in equation (3-13). It is clear that Figure 4-6 is poorly described by this, as the intensity clearly does not follow the $\sin^2(\frac{1}{2}\vec{Q} \cdot \vec{d})$ dependence predicted in equation (3-13). However, that equation describes the intensity expected from a single crystal of the material, while this experiment was performed on a powder. The neutron beam sees all orientations of the crystal, not just one, and so an average over all orientations must be performed.

For a powder of a dimer, the intensity is expected to be

$$I(q, \omega) \propto 1 - \frac{\sin(Qd)}{Qd} \delta(E - J) \quad (4-2)$$

where d is, again, the separation of the dimer.⁸⁴⁻⁸⁶ The data is accurately described by an equation of this form, and this fit is shown in Figure 4-6.

While the dimer separation R can be determined from the intensity map of Figure 4-6, but it may also be obscured by the background subtractions required to eliminate the high energy phonon. A more accurate method of obtaining R would be to perform a constant-E scan through the dispersion center at 7.7 meV. This scan is shown in Figure 4-7.

The dimer separation can then be determined by fitting the powder averaged intensity, including the V^{4+} form factor, with a linear background term representing any incoherent scattering plus any phonon beyond the range of the scan. The form factor for V^{4+} is found in Ref. 87. The whole is then fitted to an equation of the form

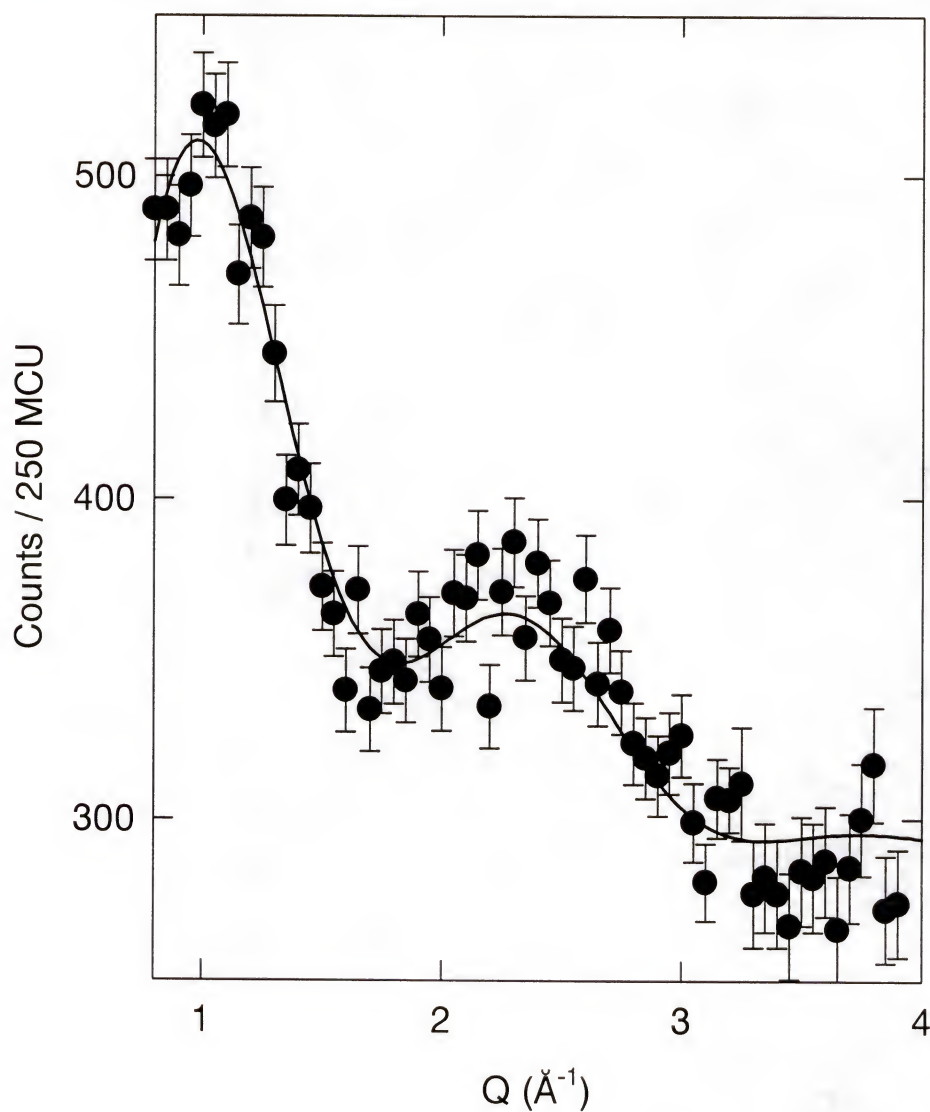


Figure 4-7 Constant-E Scan of VODPO

A constant-E scan taken of a powder sample of VODPO, at an energy transfer of 7.7 meV. The scan was performed on the HB1 spectrometer, at a temperature 10K, using a fixed final energy of 13.5 meV.

$$I(q) = A \left(1 - \frac{\sin(qR)}{qR} \right) F(q)^2 + A_1 q + A_2 \quad (4-3)$$

where A_1 and A_2 are the linear and constant backgrounds, and this fit is shown in Figure 4-7. This fit produces a dimer separation $R = 4.435(66) \text{ \AA}^{-1}$.

4.4 Conclusions

Experimental results on VODPO have confirmed some previous knowledge about the material, but have directly contradicted others. Specifically, neutron scattering confirms that VODPO is a dimer, but overturns previous ideas about the exchange path. The reasons and implications of this are discussed below.

4.4.1 Dimer confirmation in $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$

This work confirms an earlier result that VODPO is a simple dimer. Magnetic susceptibility studies⁷⁵ had been used as evidence of the dimer nature of the material. This study confirms those results.

The peak seen in Figure 4-3 is magnetic. The temperature dependence, and the agreement of the energy gap with previous results, is ample evidence of that. This magnetic peak is dispersionless, a characteristic of the dimer. A single peak is seen, with its width limited by the resolution of the spectrometer. This single peak is characteristic of the isotropic dimer. However, resolution calculations combined with the predictions of Equation (3-6) show that the observed peaks are consistent with the anisotropic dimer model for an anisotropy $\alpha = 1.0 \pm 0.2$.

With the magnetic susceptibility, dispersion, and neutron scattered intensity all fitting the isotropic dimer model, combined with chemical bond analysis,⁷³ the dimer nature of VODPO can be taken as proven.

4.4.2 Dimer exchange path in $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$

The exchange path for the dimer identified in these experiments, however, differs from the one expected. Of the two exchange paths shown in Figure 4-2(b), the expected exchange was the nearest neighbor P1 path, a V-O-V exchange with a V-V distance $d_1 = 3.0856(2) \text{ \AA}$. The P2 path, a V-O-P-O-V exchange, has a V-V separation of $d_2 = 4.3246(3) \text{ \AA}$. Other V-V separations are even greater, the next smallest separation being $d_3 = 4.8456(4) \text{ \AA}$.

The V-V separation found in Figure 4-7, with a resolution convolution included, is $4.435(66) \text{ \AA}$.¹⁴ This value is only consistent with the P2 exchange path. Since the material is a HAID, this means that the V-O-P-O-V path has a large exchange, and there is no exchange along the V-O-V path. This is not at all the expected result, and deserves some explanation.

The conventional rules for superexchange interactions⁸⁸ hold that the interaction decreases rapidly with the number of ions in the path. They note, however, that covalent compounds carry a higher exchange than expected for the number of ions. In VODPO, the P2 path goes through a PO_4 group, which appears to act as a covalent bridge for the exchange. While this helps explain why a greater than expected exchange occurs over the P2 path, it does not explain why there is so little exchange over the P1 path.

Schematics of the two pathways are shown in Figure 4-8. The bottom of the figure shows the projection of the dimer path in the a-b plane, connected schematically to the full representation at the top of the figure. The V-O-V angle of path P2 is $96.2(15)^\circ$. The two angles in path P1, the V-O-P and O-P-O angles, are $131.7(8)^\circ$ and $111.7(23)^\circ$ respectively. The V-O-V angle, being nearly 90° , would be expected to result in weak ferromagnetic exchange, while the two angles in the P1 path are sufficiently obtuse to allow greater exchange.⁸⁸

4.4.3 Role of covalent groups in magnetic exchange in $\text{VO}(\text{DPO}_4) \cdot \frac{1}{2}\text{D}_2\text{O}$

It is evident that the covalent phosphate group in VODPO plays an extremely large role in determining the magnetic interactions of the material. Conventional application of the rules of superexchange fails to note the importance of these covalent groups. They are not only important in VODPO, it appears the covalent WO_3 groups in CuWO_3 play a similarly large role in determining the magnetic properties of that material,⁸⁹ and O-Mo-O paths have been observed in FeMoO_4Cl .⁹⁰

There are cases in which covalent group do not appear to carry a strong exchange. The related material $\text{VO}(\text{HPO}_4) \cdot \frac{3}{2}\text{H}_2\text{O}$, for example, is a linear magnetic chain, with the no exchange through the PO_4 groups.⁷³

VODPO does show clearly that magnetic superexchange must be more closely examined for materials containing covalent groups. The exchange does not necessarily drop off rapidly for increasing number of ions in the path.

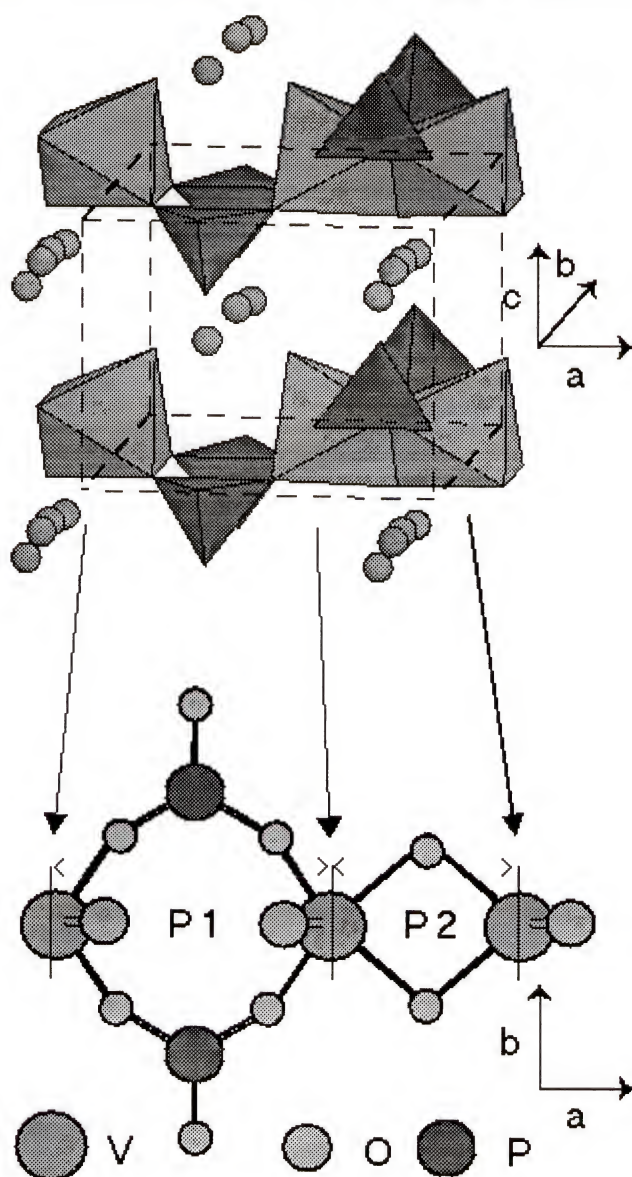


Figure 4-8 Schematic of VODPO Paths

A schematic of the magnetic exchange in the VODPO molecule. A unit cell is shown at the top, with the neighboring VO_6 octahedra joined by PO_4 tetrahedra, and these layers separated by D ions. The unit cell is connected to a schematic projection in the a - b plane, showing the exchange ions in the two possible exchange paths.

CHAPTER 5

NEUTRON SCATTERING MEASUREMENTS OF EXCITATIONS IN A POWDER OF $(\text{VO})_2\text{P}_2\text{O}_7$

Vanadyl Pyrophosphate, $(\text{VO})_2\text{P}_2\text{O}_7$ (or VOPO for short), is an industrial catalyst used in the petroleum industry, and was considered the leading candidate for a spin ladder system.⁴⁰ A series of neutron scattering experiments performed on a powder and crystal (in Chapter 6) of VOPO provides a determination of the actual magnetic exchange in the crystals.

This chapter begins with a discussion of the known properties of VOPO, both structural and magnetic, in Section 5.1. The following section, 5.2, discusses a neutron diffraction experiment on a powder sample of VOPO, and the method by which that sample was grown. Section 5.3 discusses an inelastic neutron scattering experiment on a powder sample of VOPO, and presents evidence of previously unobserved excitations. The chapter concludes in Section 5.4 with a discussion of the implications of the additional excitation.

5.1 Structure And Magnetic Exchange In $(\text{VO})_2\text{P}_2\text{O}_7$

An industrial catalyst used principally by the petroleum industry, VOPO has been studied for that reason. It attracted renewed attention when Johnston et. al.⁴⁰ suggested that the magnetic structure of VOPO might be a spin ladder. The spin ladder, in turn, was drawing attention as a quasi-one dimensional magnet, due to possibilities that low-dimensional magnetism could give insight into high- T_c superconductivity. The structure of VOPO has been measured and is presented in Section 5.1.1. The magnetic susceptibility has also been measured,⁹¹ and is equally well fit by the spin ladder or alternating chain model. The appropriate parameters of each fit are presented in Section 5.1.2.

5.1.1 Expected structure of $(\text{VO})_2\text{P}_2\text{O}_7$

The structure of VOPO has been measured, and its atomic positions determined.^{8,92} VOPO has a monoclinic structure, with space group P2_1 . Edge sharing VO_6 octahedra are separated by PO_4 tetrahedra in the b-c plane. There are structural similarities to the precursor material VODPO⁹² (see Figure 4-2), but in VOPO, the VO_6 octahedra share a corner with the next VO_6 octahedra in the $\vec{a}$ direction. The PO_4 tetrahedra also share a corner with the next PO_4 in the $\vec{a}$ direction as well, forming the pyrophosphate P_2O_7 .

A simple schematic of the VOPO structure is shown in Figure 5-1. The two magnetic structures proposed for this material are easily visible in the schematic. The proposed ladder structure is evident in the drawing, with the V^{4+} ions, located in the center of each diamond, interacting through adjacent VO_6 octahedra (represented by diamonds), and separated from their next nearest neighbors by PO_4 tetrahedra (represented by triangles). The alternating chain model proposed most notably in ref. 73 requires a large exchange over the edge joined VO_6 groups, and then a similarly large exchange over the PO_4 group. The precursor material VODPO, discussed in the previous chapter, is structurally similar to VOPO, and displays a large exchange through a PO_4 group, with minimal exchange between nearest neighbor V^{4+} ions, lending some credence to the alternating chain model.

At the time of these experiments, the spin ladder model was considered the best explanation for the properties of VOPO. This was due to the superior fits using that model to the magnetic susceptibility,⁴⁰ electron-phonon resonance,⁹³ and inelastic neutron scattering.¹¹

5.1.2 Magnetic susceptibility of $(\text{VO})_2\text{P}_2\text{O}_7$

The magnetic susceptibility of VOPO was used to provide insight into its magnetic properties. Johnston et. al. measured the magnetic susceptibility of VOPO powder from

$T=7.2\text{K}$ to 344.34K .⁴⁰ They were able to fit the measured susceptibility to both an alternating chain and a spin ladder model.

Monte Carlo studies of rings up to 16 spins in length were used to fit the measured susceptibility data in a later study.¹⁰ Acceptable fits were found once again for alternating chain and spin ladder models. The parameters were similar to those found by Johnston et.

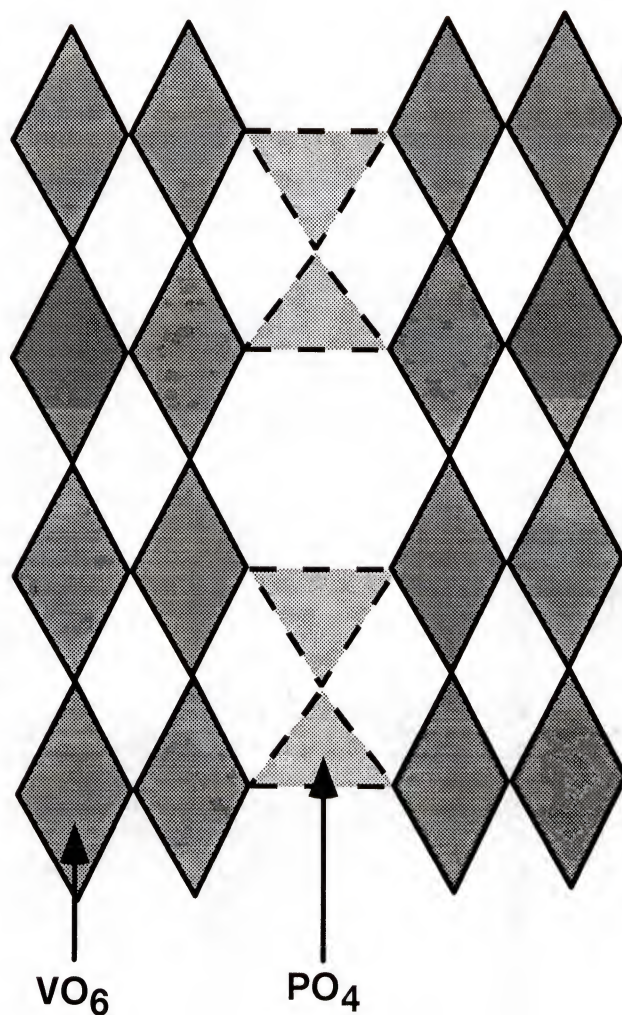


Figure 5-1 Schematic of VOPO Structure

The structure of VOPO is illustrated schematically. The dark gray diamonds represent VO_6 octahedra, which are arranged in a ladder configuration. The ladders are separated by the light gray triangles, which represent PO_4 tetrahedra.

Table 5-1 Fitted Parameters for VOPO Magnetic Susceptibility

Model	J_0 or $J_{\parallel}$ (meV)	J_1 or $J_{\perp}$ (meV)	g
Alternating Chain	11.11 (J_0)	8.02 (J_1)	1.99
Spin Ladder	7.76 ($J_{\parallel}$)	7.81 ($J_{\perp}$)	2.03

al., and are summarized in Table 5-1. The two fits were roughly identical, although the spin ladder fit was determined to be marginally better.

The fit for the spin ladder model was found to be symmetric. That is, $J_{\parallel} = J_{\perp} = J$. For this special case, it was found¹⁰ that

$$\left. \frac{E_{gap}}{J_{\parallel}} \right|_{\alpha=1} = 0.50 + 0.65(\alpha - 1) \quad (5-1)$$

$$\alpha = \frac{J_{\parallel}}{J_{\perp}}$$

Thus, for the parameters found for this fit, an energy gap of $E_{gap}=3.9$ meV was predicted.

An inelastic neutron scattering study on VOPO powder was performed using a time of flight spectrometer at the Isis Neutron Scattering Facility.¹¹ This study found a pronounced energy gap at 3.7(2) meV, in accordance with the results predicted by magnetic susceptibility studies for the spin ladder model.

Further studies of the symmetric spin ladder model were also reported, including calculations predicting the dispersion for the second and third excited modes.¹⁰ A second excitation was observed, in rough accordance with expectations for the second excited mode.

With inelastic neutron scattering data backing up theoretical predictions based on the magnetic susceptibility, the spin ladder model became the accepted explanation for the magnetic properties of VOPO.

5.2 Neutron Diffraction Experiment On $(\text{VO})_2\text{P}_2\text{O}_7$ Powder

Before beginning any inelastic scattering experiments on the VOPO powder, it was necessary to ensure the material was actually VOPO, not one of many other possible compounds. This would be done in the same manner as for the VODPO powder, by using neutron diffraction. Section 5.2.1 begins by discussing the method by which the sample was grown. The results of the neutron diffraction study are then presented in Section 5.2.2 and 5.2.3. Previous studies of the structure of VOPO^{94} provided a basis for comparison. A contaminant is also identified.

5.2.1 Growth of $(\text{VO})_2\text{P}_2\text{O}_7$ sample

As an industrial catalyst, samples of VOPO can be easily obtained. However, these are powder samples, or, at best, polycrystalline pieces. Single crystals of VOPO are difficult to grow, due in part to the large number of vanadium phosphates that can form during synthesis.

The sample of VOPO used for these experiments was prepared by first mixing stoichiometric amount of V_2O_5 (44.1 g, 99.99% pure) and $\text{NH}_4\text{H}_2\text{PO}_4$ (55.9 g, 99.9% pure) into a platinum crucible. The mixed powders were then heated to 500°C at $1^\circ\text{C}/\text{minute}$ and held at 500°C for 6 hours. This initial heating allowed the ammonia and water to escape from the crucible during the decomposition of $\text{NH}_4\text{H}_2\text{PO}_4$ to P_2O_5 . The pre-reacted mixture was then heated further to 1100°C and the resulting liquid was allowed to homogenize for several hours. The crucible was removed from the furnace and the liquid was “cast” into a shallow, cold platinum crucible. The rapid cooling of the $\text{V}_2\text{O}_5\cdot\text{P}_2\text{O}_5$ resulted in the formation of a homogenous glass with a dark green to black color. All the steps detailed above were performed in air.

The shallow crucible was placed in a tube furnace in which the partial pressure of oxygen could be controlled. A mixture of 0.1% oxygen and 99.9% argon was passed through the furnace at 40cc/minute, and this rate and partial pressure were maintained

during the entire crystal growth procedure. The $V_2O_5 \cdot P_2O_5$ glass was heated to 1050°C, maintained for 6 hours, and cooled at 1°C/hour to 480°C, after which the furnace was turned off.¹²

The resulting material consisted of several hundred small crystallites embedded in a polycrystalline base. The crystallites were smaller than 1 mm³, but could be easily removed from the base. They were pale green and translucent, consistent with VOPO coloration. The base material was dark green to black, consistent with expected color for a polycrystalline sample of VOPO.

Several hundred of the small, single crystals were removed from the base for later examination, with the expectation that they were single crystals. The base material was then ground into a fine, micron sized powder. Two samples were taken from the same container of powder. A sample of 9 g of material was placed in a vanadium cylindrical can for a neutron diffraction experiment, and 18 g were placed in an aluminum can for inelastic experiments.

5.2.2 Neutron diffraction of $(VO)_2P_2O_7$ powder

The experiment was conducted on the HB4 Spectrometer at the HFIR at ORNL, the same spectrometer that was used to determine the structure of the VODPO powder. See Figure 2-2 for a schematic diagram of the spectrometer. The spectrometer collimations used are the same as for VODPO, namely pre-monochromator - pre-sample - post-sample of 60'-60'-6'.

For the experiment, a sample consisting of 9.0 g of material was placed in a vanadium cylinder. Vanadium cylinders are ideal for diffraction experiments due to their extremely small scattering lengths, so the container can safely be neglected when analyzing the collected data. The cylinder was placed in a closed-cycle refrigerator with temperature controllable from 10K to 300K with an accuracy of ± 0.1 K. The powder data was measured at 10K and 300K.

The powder data for the VOPO sample at room temperature is shown in Figure 5-2. The observed data points are shown, along with a fit described in the following section, for the VOPO portion of the sample only. The differences between observed intensity and the calculated fit for VOPO shows clearly that there is contamination in the sample.

The contaminant was identified as $V^{3+}(PO_4)_3$, or vanadium metaphosphate. The sample was grown under flowing oxygen which would result in a lower oxygen partial pressure at the bottom of the sample tube, which in turn could result in the lower ionization of the vanadium ion.¹³ This also indicates that the small crystallites, which were at the top of the sample, were more likely to be pure VOPO.

There were no additional peaks evident at 10K, indicating no structural changes or magnetic ordering at low temperatures.

5.2.3 Rietvelt analysis and parameters

Rietvelt analysis on the powder pattern yielded structure parameters that were consistent with those found previously.⁹⁴ The parameters are shown in Table 5-2.

The observed crystal symmetry, $P2_1$, has a single identical position. A unit cell of VOPO contains 104 atoms, giving 52 unique positions. The atomic positions are shown in Appendix C.

5.3 Inelastic Neutron Scattering Experiment On $(VO)_2P_2O_7$ Powder

Inelastic neutron scattering experiments were performed upon a separate powder sample of the VOPO material. While neutron inelastic scattering experiments on VOPO powder had been performed on time of flight¹¹ neutron scattering machines, these were to be the first such experiment on a triple axis spectrometer.

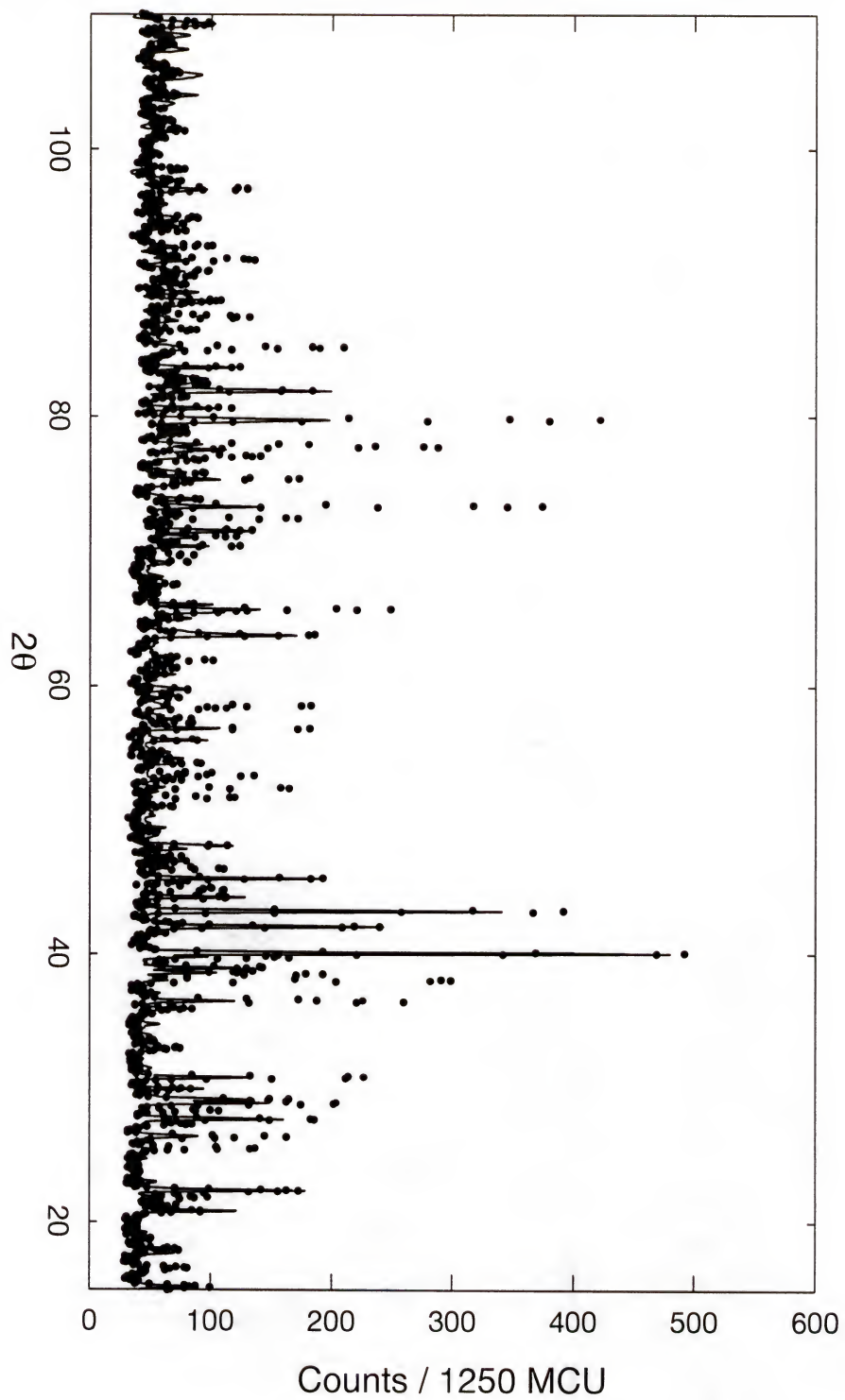


Figure 5-2 Powder Pattern for VOPO

Section 5.3.1 begins with the experimental configurations used in these experiments. The following section, 5.3.2, begins discussing the inelastic neutron scattering experiments by looking at the temperature dependence of the excitations, as well as showing the existence of two excitations where only one had been expected. The following section, 5.3.3, examines the onset of the excitations in Q by using constant energy scans. Section 5.3.4 concludes by looking at a potential high-energy excitation.

5.3.1 Spectrometer configurations and experimental setup

A sample consisting of 18.1g of VOPO powder was used in all the experiments

Table 5-2 VOPO Structural Parameters

Lattice Constant	Experimental Result (Å)	Accepted Value (Å)
a	7.85 (12)	7.727
b	16.62 (8)	16.589
c	9.41 (86)	9.580
β	89.975°	89.975°

presented here. The sample was taken from the same source as the elastic experiments, and so should be assumed to have the same makeup, 97% VOPO, 3% vanadium metaphosphate. For the experiments at HB1A, the powder was placed in a closed-cycle refrigerator, with the temperature controllable from 10K to 300K with an accuracy of ± 0.1 K. The experiments at HB3 were performed using a Helium cryostat, with temperature controllable from 1.5K to 300K with an accuracy of ± 0.1 K.

Two spectrometers were used on these experiments, the HB1A spectrometer (Figure 2-3) and the HB3 spectrometer (Figure 2-4), both at the High Flux Isotope

Table 5-3 Spectrometer Configurations for VOPO Powder

Spectrometer	Pre-Mono.	Pre-Sample	Post-Sample	Post-Anal.
HB1A	40'	40'	40'	70'
HB1A	40'	20'	20'	70'
HB3	40'	40'	40'	120'

Reactor at Oak Ridge National Laboratory. The HB1A spectrometer provides a beam with fixed incident energy of 14.7 meV, while the experiment at HB3 uses a fixed final energy of 14.7 meV. The collimations used at the two spectrometers are noted in Table 5-3. Two different configurations were used at the HB1A spectrometer, and both are noted.

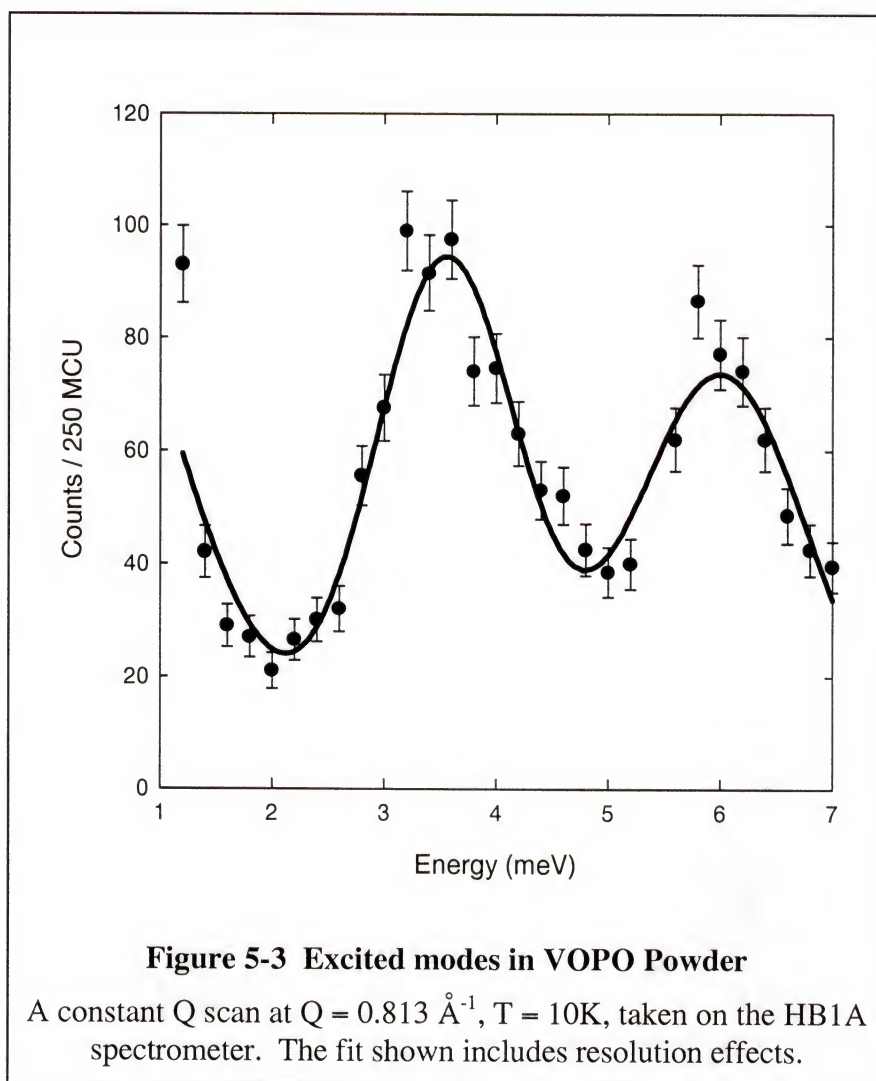
For a powder sample on a one dimensional or quasi-one dimensional material, whether an alternating chain or a spin ladder, the momentum transfer $Q = |\vec{Q}|$ does not correspond to the momentum of the excitation k . Rather, k is the projection of $\vec{Q}$ on the chain axis. So, in a powder, all 1-D modes with the observed energy transfer and $Q \geq k$ are seen. While this has minimal effect on a constant- Q scan, it makes interpretation of constant- E scans difficult. The first peak observed in a constant- E scan is unambiguous, but any features above that value contain information from the lower modes. This applies only to powders, not to single crystals, but it does provide a limit to the information available from experiments on powders.

5.3.2 Inelastic neutron scattering on VOPO powder

Excited modes were observed at $q = 0.813 \text{ \AA}^{-1}$, as expected from previous experiments. This value corresponds to $Q = 2\pi/a$, where a is the lattice parameter in the $\vec{a}$ direction, so $a/2$ is the distance between rungs on the ladder. The observed modes are shown in Figure 5-3 as observed at HB1A at $T=10\text{K}$. The most notable feature in this graph is the existence of a second mode, not previously observed. The first excited mode,

observed at 3.5 meV, agrees with previously reported values.¹¹ The second mode, at 6.0 meV, does not. The mode at 6.0 meV is also inconsistent with calculated values for the second excited mode.¹⁰

This cast serious doubt on the identification of VOPO as a spin ladder, as the



second mode did not appear within the theory for it.⁹⁵⁻¹⁰⁰ While this feature had not been previously reported, the data from the time of flight neutron experiments¹¹ do contain a

band of increased intensity consistent with this feature. The feature was not reported, perhaps, because it was not as intense as the first excitation, nor was it expected.

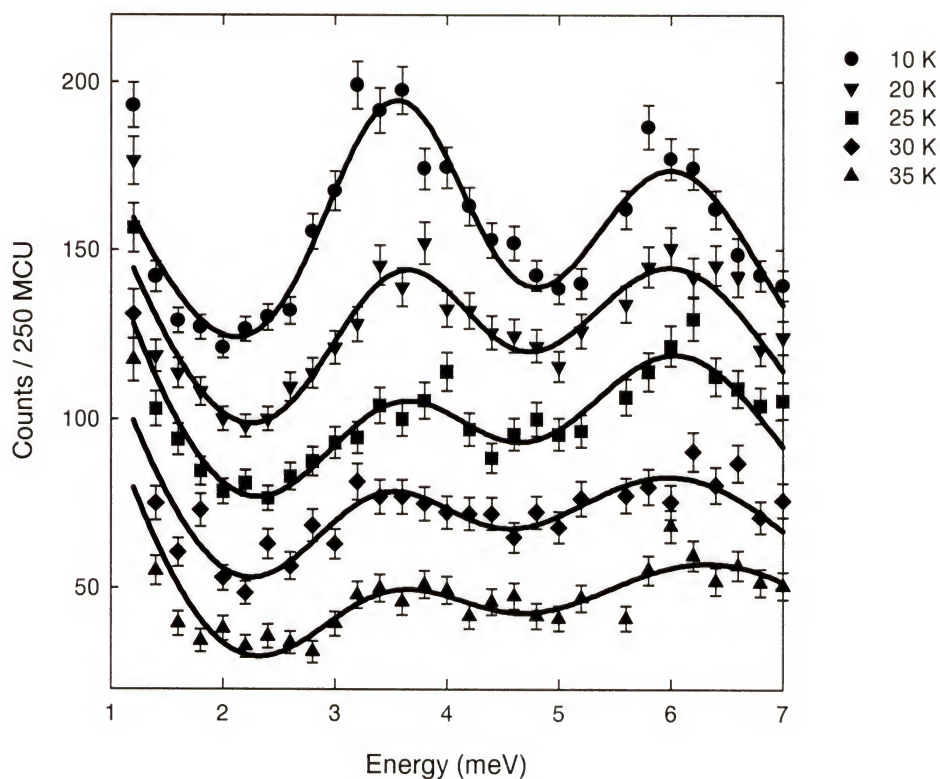
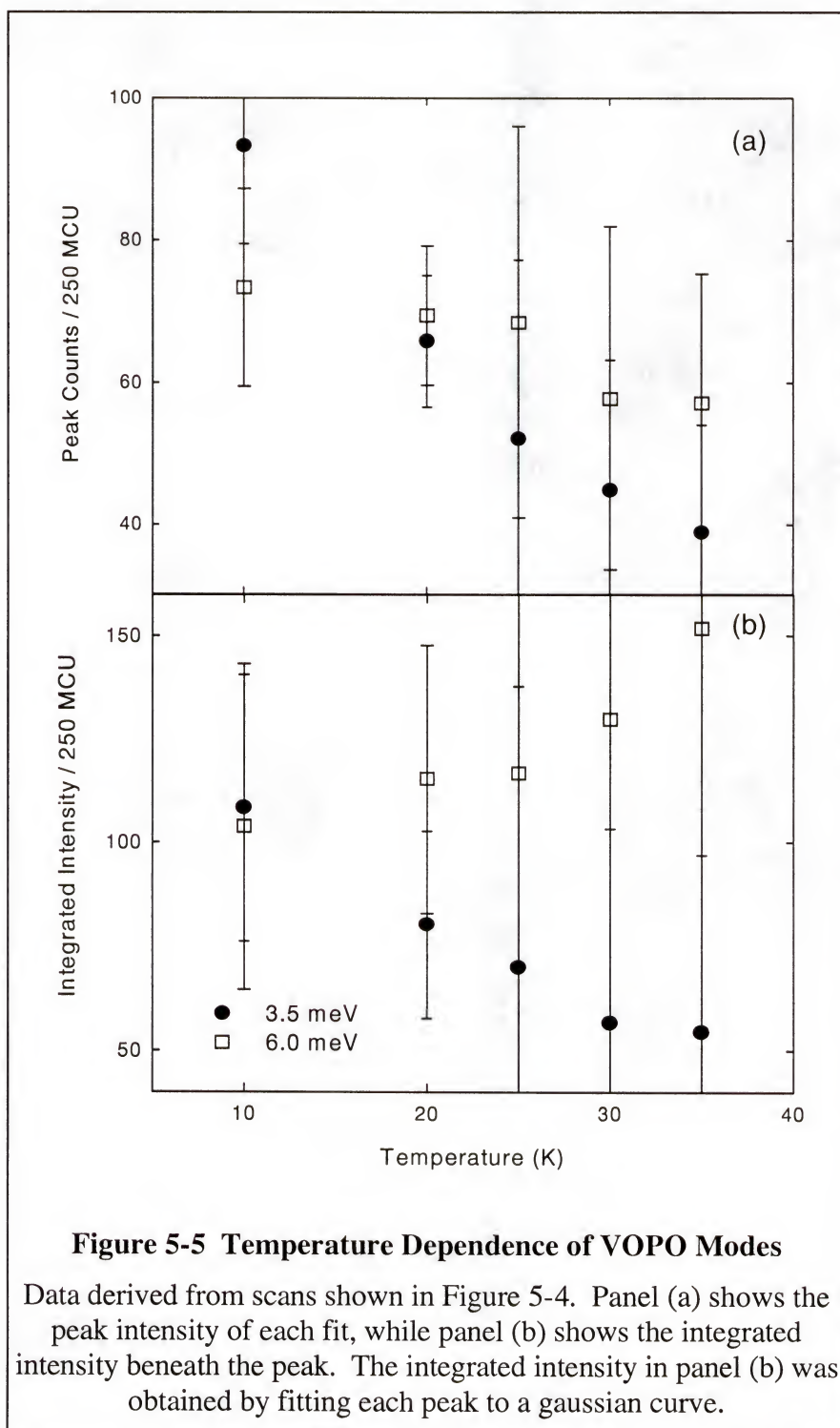


Figure 5-4 Excited modes in VOPO Powder at Varying Temperatures

A series of constant Q scans all taken at $Q = 0.813 \text{ \AA}^{-1}$, on the HB1A spectrometer. Each successive scan has a constant background of 25 counts added to it for clarity of presentation. The fits shown include resolution.

It was necessary to confirm that both modes were magnetic before drawing conclusions about the properties of VOPO. The peak intensity of a magnetic mode will decrease with temperature, although the integrated intensity should remain constant⁸². By contrast, both peak and integrated intensity from a phonon mode will increase with

temperature.⁸³ A magnetic mode will also lose intensity at higher values of Q , but that was not easily observed in this experiment for kinematic reasons. A series of scans at $Q = 0.813\text{\AA}^{-1}$ at different temperatures is shown in Figure 5-4.



The temperature dependence of the peaks is shown in Figure 5-5. The peak intensity of each mode is plotted against increasing temperature in the upper panel. It can be seen that the upper mode, at 6.0 meV, decreases more slowly than the lower mode, staying nearly constant within the error of the experiment. The lower panel shows the integrated intensity of each peak, and both remain constant within error.

5.3.3 Constant energy inelastic neutron scans on VOPO powder

While both observed modes appeared to be magnetic in origin, it was not certain that both peaks arose from the ladder or chain excitations. Determining the onset of the two modes in Q would provide a simple resolution to that question. A constant- E scan presents difficulties in analysis, as discussed above, but it is unambiguous about the onset of the first peak. Thus, constant- E scans were performed at the mode energies, 3.5 meV and 6.0 meV, and these are shown in Figure 5-6.

As seen, both modes have a peak at $0.813 \text{ \AA}^{-1}$, as expected from previous experiments.¹¹ There is a second broad increase at $Q = 4\pi/a$, which corresponds to the structural zone center. The consistency between the two modes argues strongly that they have the same origin, and that it is magnetic. The onset of the peak occurs at $0.76 \text{ \AA}^{-1}$, which corresponds to $Q = 4\pi/b$, where $b/4$ is the average separation between V^{4+} ions in the crystal $\vec{b}$ direction.

5.3.4 High energy excitations in VOPO powder

While the existence and magnetic origin of the two lower modes at 3.5 meV and 6.0 meV have been shown clearly, an additional, high energy excitation consistent with predictions for 2-magnon modes in the symmetric spin ladder model had been reported using TOF neutron scattering.¹¹ In order to examine this mode on the triple axis spectrometer, a fixed final energy, instead of a fixed initial energy, was necessary. These experiments were performed on the HB3 spectrometer, where this option was available.

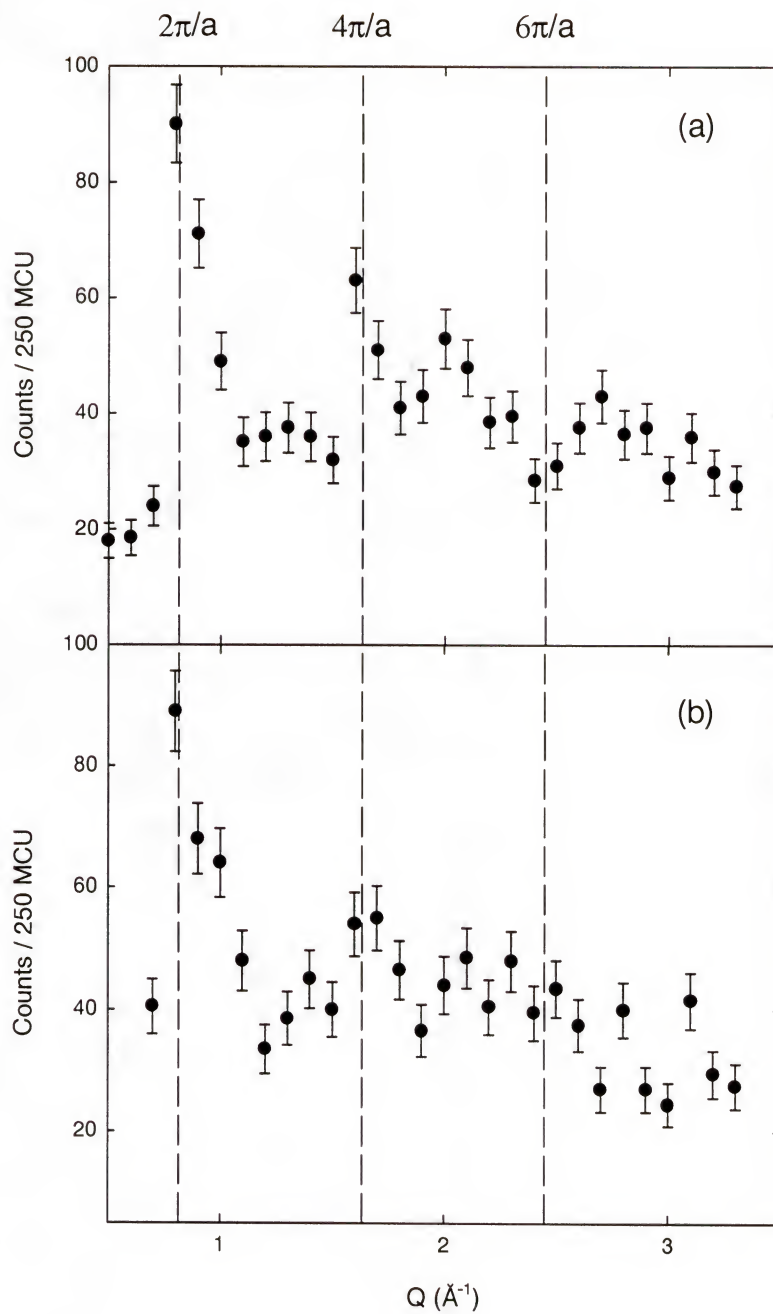


Figure 5-6 Constant Energy Scans on VOPO

Constant energy scans at 3.5 meV (a) and 6.0 meV (b), taken at the HB3 spectrometer with a final energy $E_f = 14.7$ meV. Both scans were taken at $T=1.5$ K.

The resulting data was very unclear, due partly to the decreased resolution, and partly to phonons that occurred at higher energies. However, phonon excitations do not change as q increases, while magnetic excitations do. Thus, by examining the scattering at 2 constant- Q scans, one at $Q=3\pi/a$, and one at $Q=5\pi/a$, and subtracting the second from the first, only magnetic scattering should remain. The results of this, along with the original data, are shown in Figure 5-7.

A broad upper mode is visible, centered at $E = 15$ meV. This is roughly consistent with calculated values for the two-magnon mode for a symmetric spin ladder.¹⁰

5.4 Conclusions

While these experiments on a VOPO powder confirmed some previous work, they raised a new and very important question. Specifically, the existence of an excitation at 6.0 meV had not been previously reported, nor was it easily explained.

The excitations observed by Eccleston et. Al. in Ref. 11. were observed in these experiments. An energy gap of 3.5 meV, with an onset of $0.8 \text{ \AA}^{-1}$ is clearly seen throughout these experiments, see Figure 5-3 and Figure 5-6. A higher excitation at roughly 13 meV can be observed in Figure 5-7. These are consistent with the 3.7 meV and 14 meV excitations reported by Eccleston.

The remaining excitation at 6.0 meV had not been reported in any previous work. Theoretical calculations based on the spin ladder Hamiltonian¹⁰ did not predict any intermediate excitations between the bound 1 and 2 magnon modes. The predicted dispersion, using the exchange constant J and lattice parameter a found in these experiments, is shown in Figure 3-9.

Three possible explanations for the existence of the 6.0 meV excitation present themselves. First, it could be a crystal field excitation of the V^{4+} ion. Second, it could be the result of spin anisotropy, or third, there could be an error in the model applied to the system.

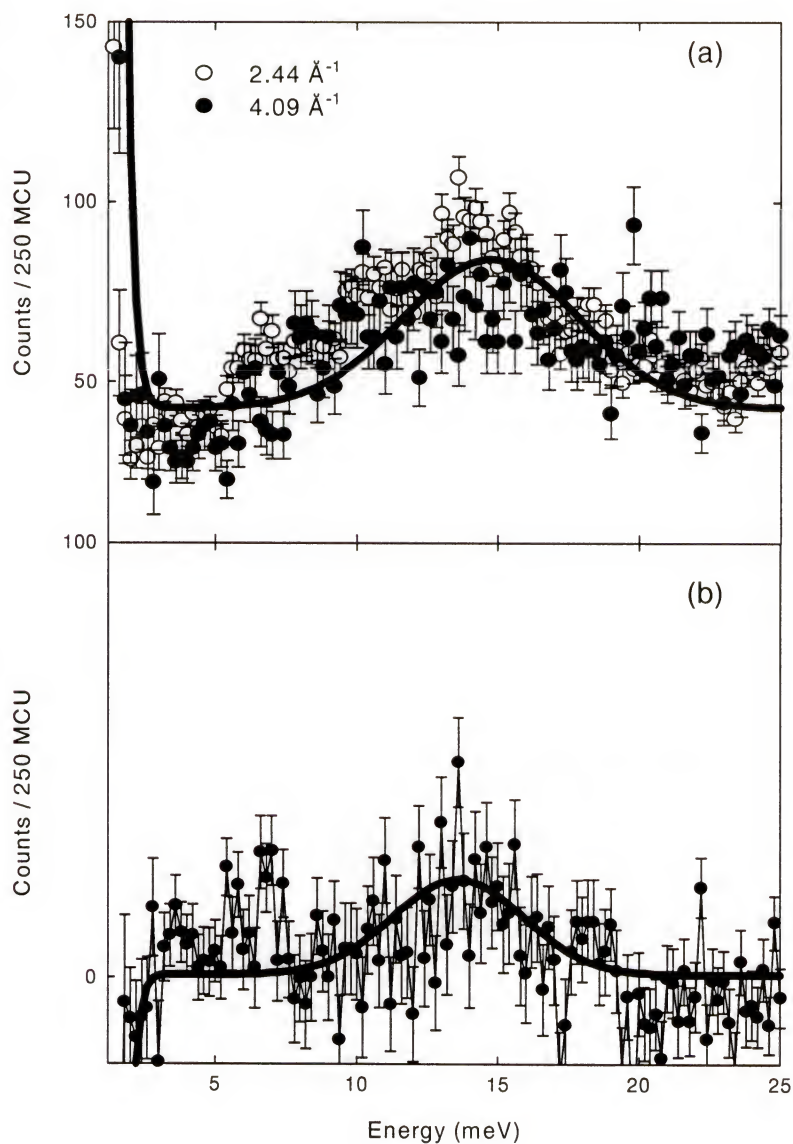


Figure 5-7 VOPo Powder High Energy Mode

Panel (a) shows two constant Q scans, taken at $Q = 2.44 \text{ \AA}^{-1}$ and $4.07 \text{ \AA}^{-1}$, corresponding to the centers of the 2nd and 3rd magnetic zones. Both scans were taken at $T = 1.5\text{K}$, at the HB3 spectrometer, with final energy $E_f = 14.7 \text{ meV}$. Panel (b) shows the difference between the two scans, revealing additional scattering intensity centered at 13 meV. All fits shown are merely guides to the eye.

The crystal field of an isolated V^{4+} ion in an octahedral field is a triplet that can be split by spin-orbit interactions or departure from octahedral symmetry. Isolated V^{4+} ions in ruby have excited states at 3.5 meV and 6.6 meV,¹⁰¹ which raises the possibility that either or both of the observed excitations might originate in the crystal field levels. However, crystal fields are generally independent of Q , while Figure 5-6 shows a strong Q dependence.

Spin anisotropy is another possible explanation for the 6.0 meV mode. Anisotropy could split an otherwise degenerate level into the two observed excitations. However, doing so, with the symmetric spin ladder model, would increase the value of the exchange constant J ($\sim 2E_{\text{gap}}$ by $(5-1)$), thereby disagreeing with the value observed in magnetic susceptibility experiments. Further, the same magnetic susceptibility data was consistent with a g -value of 2, which indicates isotropic spin coupling.

The final possibility, and by far the most interesting, was an error in the model. Either a bound mode existed in the spin ladder Hamiltonian that had previously been unobserved, or the spin ladder Hamiltonian was inappropriate for VOPO. It was unclear whether a bound mode would exist in the alternating chain model.

CHAPTER 6

NEUTRON SCATTERING MEASUREMENTS OF EXCITATIONS IN A CRYSTAL ARRAY OF $(\text{VO})_2\text{P}_2\text{O}_7$

Additional information about the excitations of VOPO required a large single crystal, or an aligned array of small single crystals, which is the approach taken on these experiments. This chapter begins in Section 6.1 with a description of the array of crystals designed for these experiments, and a determination of the mosaic of the completed array. The following section, 6.2, describes a series of inelastic neutron scattering scans on the crystal array, along with the excitations observed in the scans. In the next section, 6.3, a dispersion curve for VOPO is developed from the inelastic neutron scans, which shows the nature of the magnetic exchange in VOPO. Section 6.4 concludes with a description of the magnetic exchange, as well as those details about the exchange that remain unclear.

6.1 Description And Preparation Of Array Of $(\text{VO})_2\text{P}_2\text{O}_7$ Crystallites

In order to gain more information about the magnetic properties of VOPO, a single crystal of the material was necessary. A single crystal would permit examination of the magnetic properties along specific crystal axes, which would allow the determination of the material's magnetic dispersion. However, single crystals of VOPO of sufficient size to allow inelastic neutron scattering did not exist.

The solution to this problem rested with the many small crystallites in the sample discussed in the preceding chapter. X-ray scattering and visual examination led to the belief that these small crystallites were single crystals. If properly aligned, a large number of them could be used as a single crystal of the material. This section describes the methods used to align these crystallites, and examines the mosaic of the resulting array.

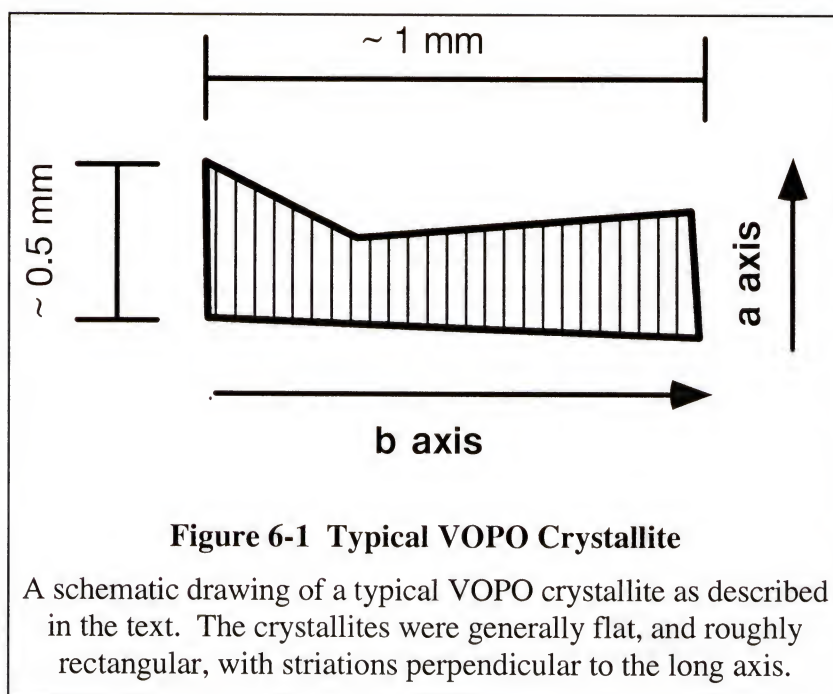
6.1.1 (VO)₂P₂O₇ crystallite shape and alignment

The crystallites average volume was less than $\frac{1}{4}$ mm³. They were generally rectangular in shape, rarely longer than 1 mm in the longest direction, while less than $\frac{1}{2}$ mm in thickness. The average mass of a single crystallite was ~0.004g. It would take 200 or more such crystallites to produce a mass sufficient for inelastic neutron experiments. As such, it was necessary to be able to determine the crystal axes without subjecting each individual crystallite to x-ray scattering.

Two features of the crystallites provided visual cues to the crystal axes. First, the crystals were generally flat, and the thin axis in crystals can often be expected to correspond to a crystal axis. While many crystals were rectangular, there was sufficient variation that a long axis could not be reliably determined. However, striations occurred on the surface of the crystals in all cases. In those crystallites with a clear rectangular shape, the striations ran perpendicular to the long axis. These were the second feature that could indicate a crystal axis. A drawing of a typical crystallite is provided in Figure 6-1.

The crystal axes of a few, sample crystallites were determined on an x-ray powder diffractometer. The crystal sample was placed on a sample tray located at the center of rotation of the instrument. The crystal was oriented by hand, using the two crystallite features noted above. A radial scan was taken, and resulting Bragg peaks were analyzed to determine which axis was being observed. If no peaks were observed, the crystallite could be turned slightly, and the process repeated.

The results of these scans were consistent across each of 5 sample crystallites. The thin axis of the crystallite could be identified as the crystal c axis, while the surface striations were parallel to the crystal a axis. This permitted the alignment of a large number of crystallites.

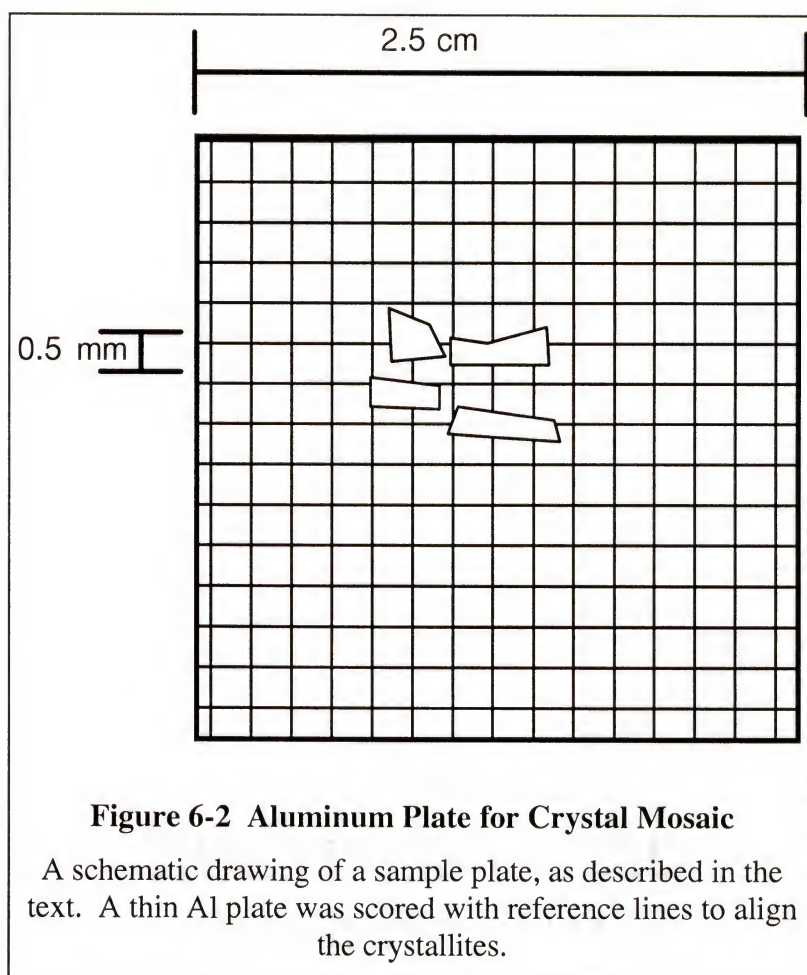


6.1.2 Development of arrays of $(\text{VO})_2\text{P}_2\text{O}_7$ crystallites

The arrays of crystallites were prepared by placing 30-50 crystallites on a small, thin, aluminum plate. The plates were made of aluminum, 2.5cm x 2.5cm x 0.1mm. The plates were then scored with lines running parallel to its edges, spaced 0.5mm apart, in order to have a guide against which to align the crystallites. A schematic of the sample plate is shown in Figure 6-2.

The crystallites were aligned under a microscope, and attached to the plate using Duco Cement. This adhesive contains hydrogen, which would interfere with neutron scattering. In order to have the minimum possible amount of adhesive in the beam, it was diluted with acetone before being used to fasten the crystallite to the plate.

In order to ensure the maximum concentration of material stayed in the beam, the crystals were placed in the center of the plate. As more crystals were added, they were added radially outwards, giving a roughly circular appearance to each array.



6.1.3 Determination of mosaic of $(\text{VO})_2\text{P}_2\text{O}_7$ crystal arrays

Before beginning inelastic experiments, it was necessary to determine the mosaic of the array, to find out how well these crystallites were aligned. The HB1A spectrometer at the HFIR was used for this purpose, with collimations noted in the following section, Table 6-1.

The plates were examined both individually and combined. All these experiments were performed at room temperature, 300K, and used the (2 0 0) and (0 4 0) Bragg peaks, due to their large intensities.

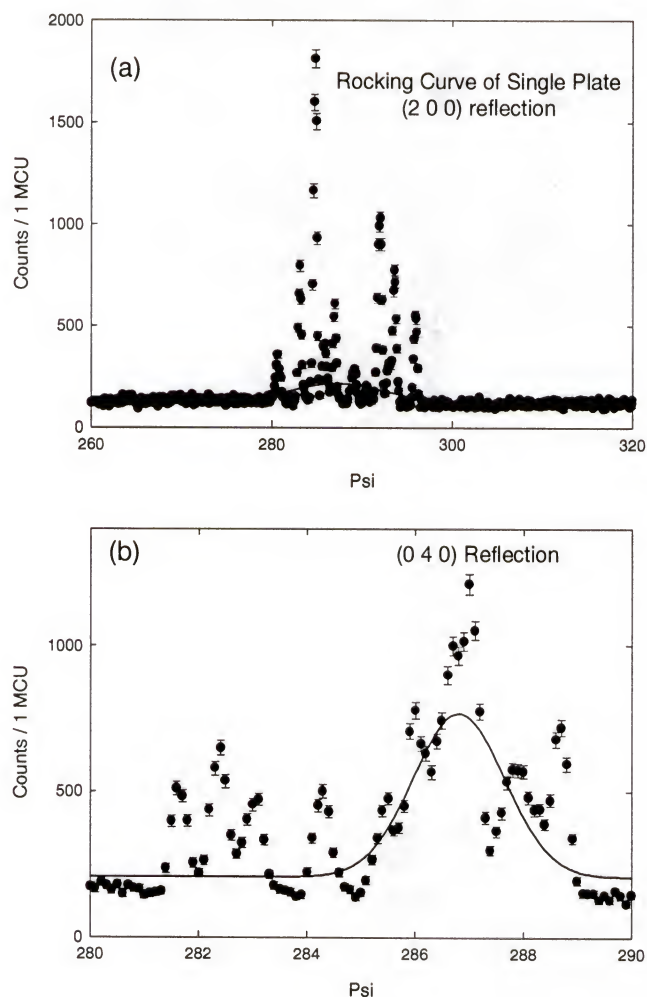


Figure 6-3 Mosaic of a Single Plate Array

An elastic neutron scattering scan of a single sample plate as described in the text. The sample plate angle ψ alone was rotated. The experiments were performed on the HB1A spectrometer at room temperature. The (0 2 0) and (0 4 0) peaks shown in panel (a) and (b), respectively, are perpendicular, however, the sample was turned by hand, so the angles shown on the drawing are not displaced.

6.1.3.1 Individual plates of the $(\text{VO})_2\text{P}_2\text{O}_7$ crystal array

Each of the six plates were first examined individually, using the HB1A spectrometer, with a fixed incident energy of 14.7 meV. The spectrometer was aligned to observe the expected (2 0 0) or (0 4 0) Bragg peak, and only the sample angle ψ was rotated. The results for one plate are shown in Figure 6-3, for the two peaks used.

The scans show numerous small, sharp peaks, spread out over 5-15°. The sharp peaks are likely the result of scattering from single crystallites, while the spread is a result of the imperfect alignment of those crystals on the plate. The sharp peaks have a half-width of roughly 0.2°, representative of a perfect single crystal. A gaussian fit to the data, while a poor description, can be used to get an effective mosaic for each plate, 7.3° in Figure 6-3.

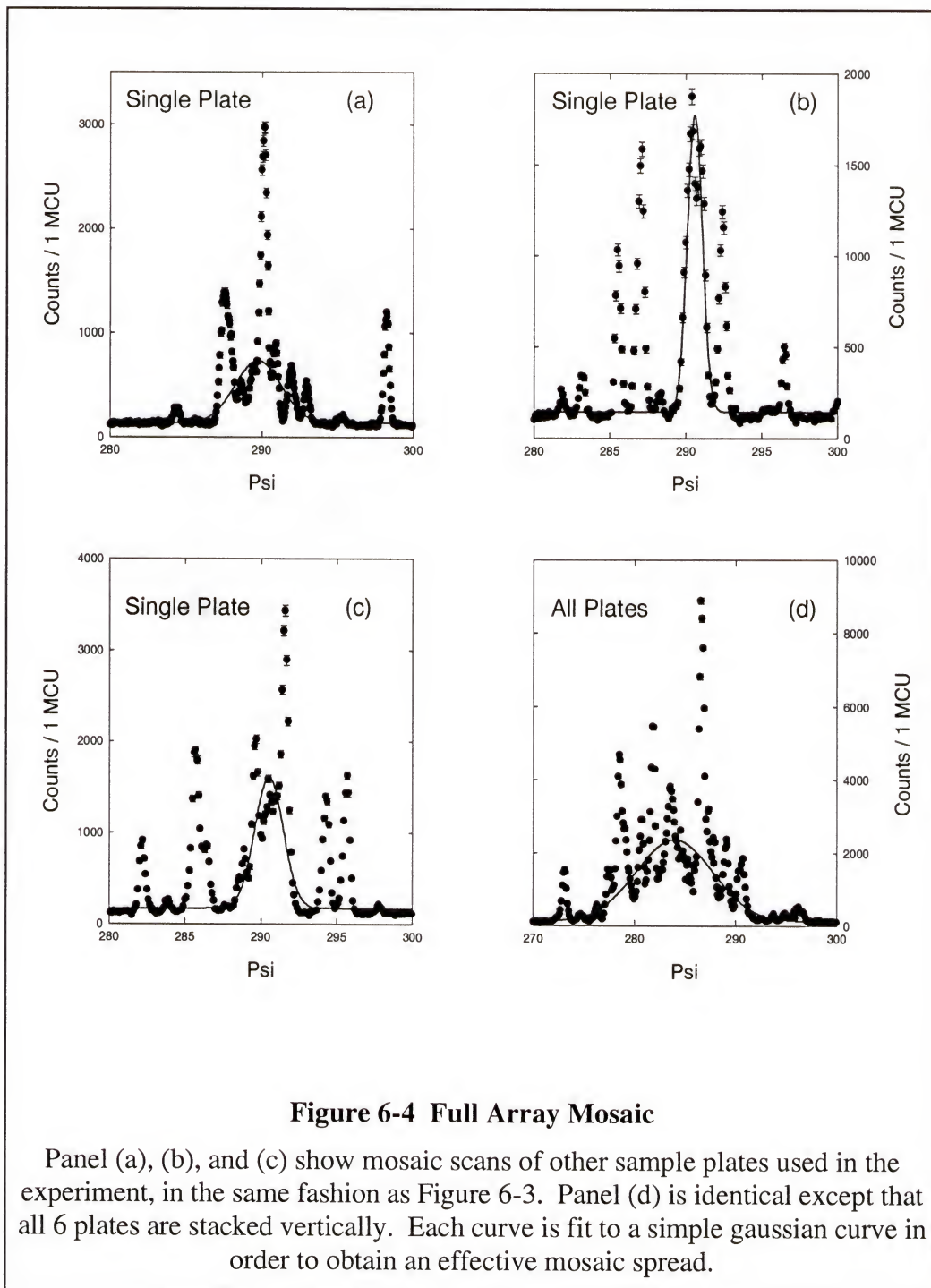
6.1.3.2 $(\text{VO})_2\text{P}_2\text{O}_7$ crystal array

The graphs in Figure 6-4 show the scattering from three other individual plates (Figure 6-4(a-c)), and all 6 plates aligned and stacked vertically (Figure 6-4(d)). All four scans are shown in the (2 0 0) reflection. The array shown in Figure 6-4(d) is the sample used for all the experiments reported in the remainder of this chapter. In total, it consists of roughly 200 crystallites, with a sample mass of roughly 1g.

The mosaic for the full array continues to show the prominent sharp peaks that are characteristic of individual crystallites. As in the case of the individual plates, a gaussian curve can be fit to the scattering from the full array, which yields an effective mosaic of 9.6° for the array as a whole.

Because of the wide mosaic, and sharp individual peaks, some conventions were applied in aligning the array throughout the following experiments. The crystal would be lined up using two perpendicular, intense Bragg peaks. Specifically, the (2 0 0) peak shown above, and the (0 4 0) peak. A rocking curve, similar to that in Figure 6-4, was taken for each peak, and a gaussian curve was fitted to the results.

The sample would be oriented such that the Bragg peak would be near the center of the gaussian fit, but offset from that center to the most intense of the sharp peaks. The



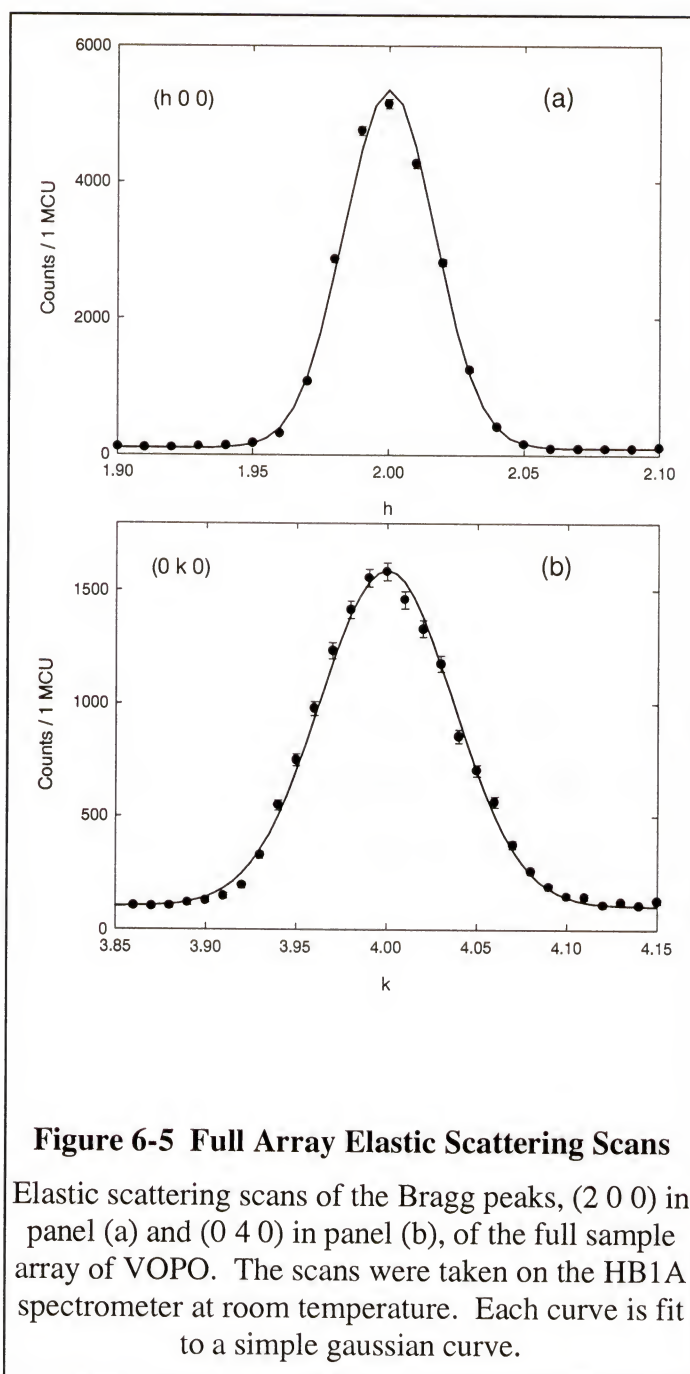
peak center chosen would not be more than 0.5° from the center of the fit. This would provide a strong central background from many overlapping peaks, while still allowing a strong Bragg peak for purposes of ensuring the array was properly aligned.

Typical Bragg scattering scans for the whole array are shown in Figure 6-5. The peaks in the (2 0 0) and the (0 4 0) are shown, with a gaussian fit also displayed. The fitted half widths are 0.08° and 0.11° respectively. The narrowness of these peaks provides further evidence that, at least along principal axes, the array acts as a single crystal.

6.2 Inelastic Neutron Scattering Experiment On $(\text{VO})_2\text{P}_2\text{O}_7$ Crystal Array

The crystal array was used for inelastic neutron scattering. The purpose of these experiments was to determine the dispersion of the magnetic modes that had been observed in the powder of the material. The large mosaic in the array would not have a large effect as long as the scattered vector lay close to one of the reciprocal axes. While this was a limit, it would at least allow observation of the dispersion along the three crystal axes.

This section begins with a description of the three spectrometers and the configurations of the spectrometers used in these experiments. The two excitations that were observed in the powder data, and these are shown in the Section 6.2.2. Following that the temperature dependence of the peaks is examined in Section 6.2.3 to ensure these are both magnetic in nature. In Section 6.2.4, the excitations are then examined at different values of Q to observe the dispersion. Finally, in Section 6.2.5, the high energy excitations near the zone boundary in the crystal $\vec{b}^*$ direction are examined, and tested in their temperature and Q dependence to ensure they are magnetic.



6.2.1 Spectrometer configuration and experimental setup

These experiments were performed on the HB1, HB1A, and HB3 spectrometers at HFIR. The details of these spectrometers have been explained in previous sections, see

Table 6-1 Spectrometer Collimations

Spectrometer	Pre-Monochromator	Pre-Sample	Post-Sample	Post-Analyzer	Energy Used (meV)
HB1A	40′	40′	40′	68′	$E_i = 14.67$
HB1	50′	40′	40′	120′	$E_f = 13.6$
HB1	50′	40′	60′	120′	$E_f = 13.6$
HB3	50′	40′	60′	120′	$E_f = 14.7,$ 30.5

specifically Figure 2-4 and Figure 2-3. The collimations used at the three spectrometers are shown in Table 6-1.

The array was placed in either a closed-cycle refrigerator or a helium cryostat for the experiments. The temperature in either case could be controlled to 0.1K, with a range from 10K to 300K or 1K to 300K respectively.

6.2.2 Inelastic neutron scattering excitations

The 2 modes observed in the powder data at 3.5 meV and 6.0 meV were easily observed in the crystal array as well. Figure 6-6 shows some sample scans showing those peaks in the array. The peaks shown are the (1 -2 0) and the (0.9 2 0), both from HB1 at 10K. The fits shown are a full resolution convolution, using the dispersion shown later in this chapter.

Several features are notable from these scans. The first is the simplest, that the array displays the same features as the powder of the material. This is strong evidence that the array, despite the large mosaic, is suitable for performing these experiments.

The second notable feature is that the peak locations have shifted from their position in the powder. The lowest excitation occurs at 4.1 meV, while the next excitation is at 7.2 meV. This indicates that there is dispersion in the sample. It also indicates a problem with the spin ladder model, as the magnetic zone center would be expected to occur at the $(1\ 2\ 0)$ peak.

The final feature to be noted about the scan in Figure 6-6 is that the $(1\ -2\ 0)$ and $(1\ +2\ 0)$ should be identical points. Panel (b) shows the $(0.9\ +2\ 0)$, and the peak locations have shifted, slightly, from their positions at $(1\ -2\ 0)$, indicating that it is possible to measure the dispersion of VOPO using this crystal array.

6.2.3 Temperature dependence of excitations

As with the powder data, it is necessary to verify that the observed modes are magnetic in nature. Again, temperature dependence is a simple and reliable way of checking that behavior^{82,83}. Figure 6-8 shows the $(1\ -2\ 0)$ peak at 10K, 20K, 30K, and 45K, as measured on the HB1A spectrometer. The rapid decrease in peak intensity for both excitations provides evidence that they are magnetic.

The fits shown on Figure 6-8 are simple gaussians. A full fit with resolution was only possible for the 10K data in panel (a), so the same fit was shown in each panel for consistency. The lower oscillation, at ~ 4 meV, has virtually disappeared at 20K in panel (b), while the upper excitation at ~ 7 meV is still visible at 30K. This behavior is consistent with the observed behavior of the powder, shown in Figure 5-5.

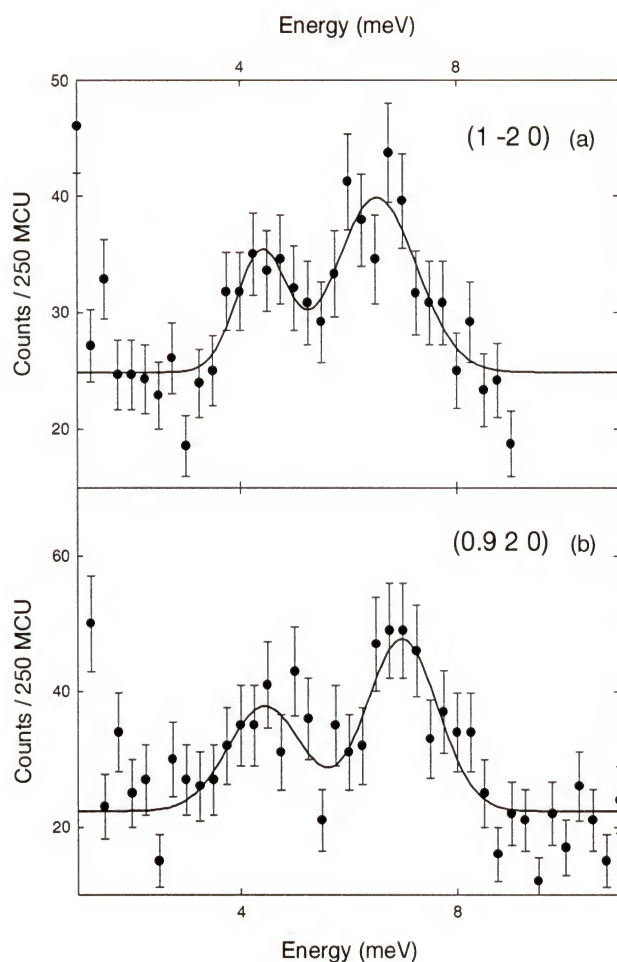


Figure 6-6 Sample Inelastic Scans on Crystal Array

Constant-Q scans of the VOPO sample array taken on the HB1 spectrometer with fixed final energy of 14.5 meV, at a temperature of 10K. The scans shown are for the (1 -2 0) in panel (a) and the (0.9 2 0) in panel (b) peaks, and are fit including resolution convolution.

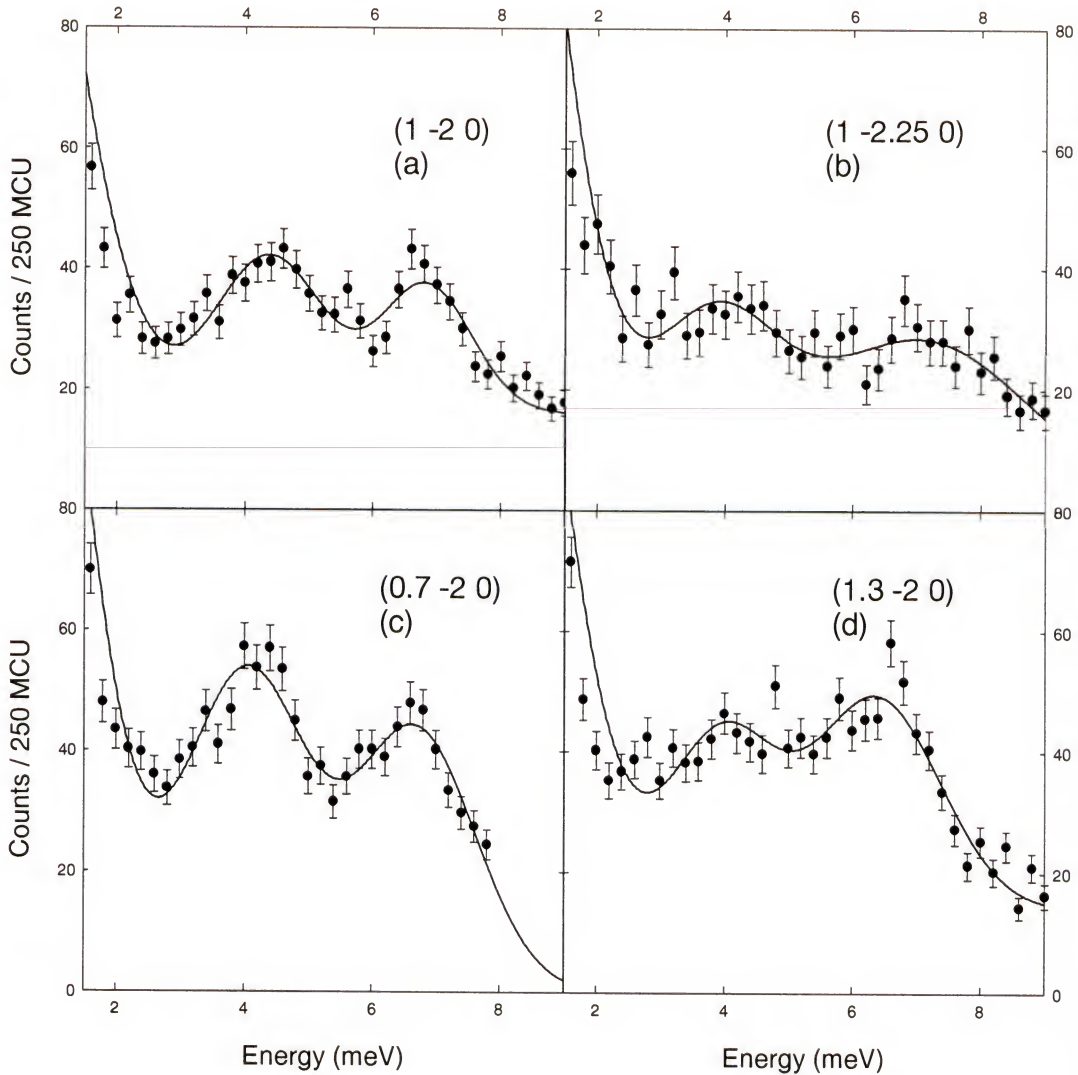


Figure 6-7 Inelastic Scans of VOPO Array

A series of constant-Q scans of the VOPO crystal array taken at HB3 with a fixed final energy of 14.7 meV at 1.5K. Using panel (a) as a baseline, the remaining panels show notable features about the VOPO dispersion as described in the text.

6.2.4 Q-dependence of excitations

Additional scans at various wavevectors are shown in Figure 6-7. The two peaks can be observed in all 4 scans. The peak intensity falls for scans further from a crystal axis.

A notable feature of Figure 6-7 is the low peak intensity in the $(1 -2.25 0)$ scan (Figure 6-7(b)). The peaks are very ill-defined, especially the higher excitation, which the fit (full resolution convolution) places at 7.8 meV, but which is questionable from the data. This occurs because of the steep dispersion in the $\vec{b}$ direction, which would create broad peaks. When combined with the large mosaic of the sample, this makes determination of the excitation energy difficult in the $\vec{b}$ direction.

Panels (c) and (d) show the $(0.7 -2 0)$ and $(1.3 -2 0)$ peaks respectively. These two peaks are both 0.3 from the expected zone center in the $\vec{a}$ direction. They both show the excitations at the same energies, 4.1 meV and 6.3 meV. However, the intensity of the excitations in panel (d) is much lower. This is a result of the large mosaic of the array.

Figure 6-7 also gives some insight into the dispersion. Panel (a) shows the $(1 -2 0)$, while each of the other 3 panels is only slightly removed from that location. In the $\vec{b}^*$ direction, as seen in panel (b), the excitation centers occur at higher energies than at the zone center. However, in the $\vec{a}^*$ direction, the excitations occur at lower energies than in the center. That is characteristic of ferromagnetic exchange, not antiferromagnetic.

A fuller picture of the dispersion is provided in Figure 6-9 to Figure 6-11, in which constant- $\vec{Q}$ scans are shown for many different values of $\vec{Q}$. Figure 6-9 shows the constant- $\vec{Q}$ scans taken in the crystal $\vec{b}^*$ direction. The error in the peak positions increases rapidly, as the intensity in the peaks falls off very rapidly. This is caused by two effects. First, the large crystal mosaic greatly decreases the resolution of scans far from a crystal axis, as is true for all scans shown. Second, the dispersion in the $\vec{b}^*$ direction is very large, which causes a further loss of resolution away from the zone center at $(1 -2 0)$.

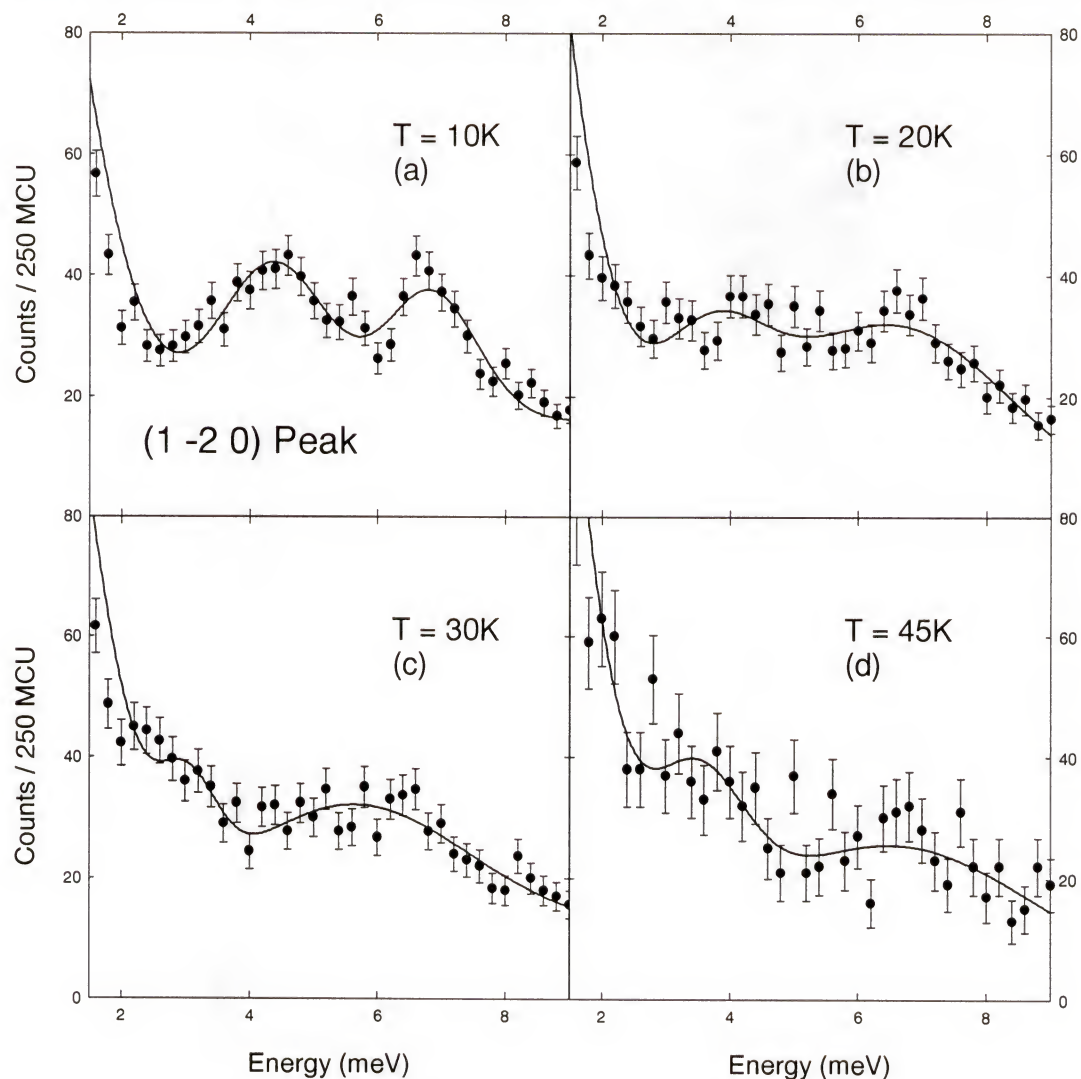


Figure 6-8 Temperature Dependence of VOPO Peaks

A series of constant-Q scans taken on the HB1A spectrometer. Panels (a) to (d) show scans of increasing temperature, and are fit using a sum of 3 gaussians.

The two figures Figure 6-10 and Figure 6-11 show the constant Q scans taken in the crystal $\vec{a}^*$ direction, from (0 -2 0) to (1.2 -2 0). A notable feature is the great reduction in peak intensity from (0 -2 0) to (1.2 -2 0). This is caused largely by the crystal array mosaic, as the scans move off of a crystal axis.

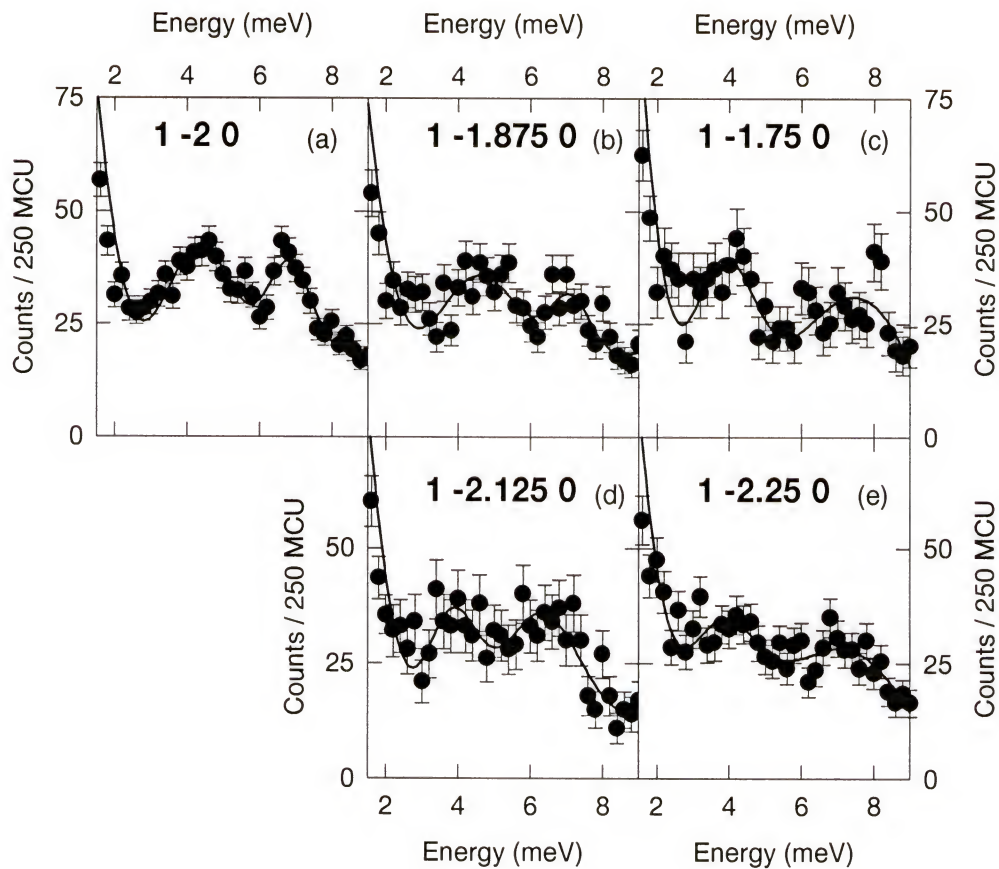


Figure 6-9 Constant Q Scans in the VOPO Crystal b^* Direction

A series of constant Q scans (a-e) of the VOPO crystal array, taken at the HB1A spectrometer with fixed $E_i = 14.7$ meV. The peak locations increase rapidly away from the zone center at $(1 -2 0)$.

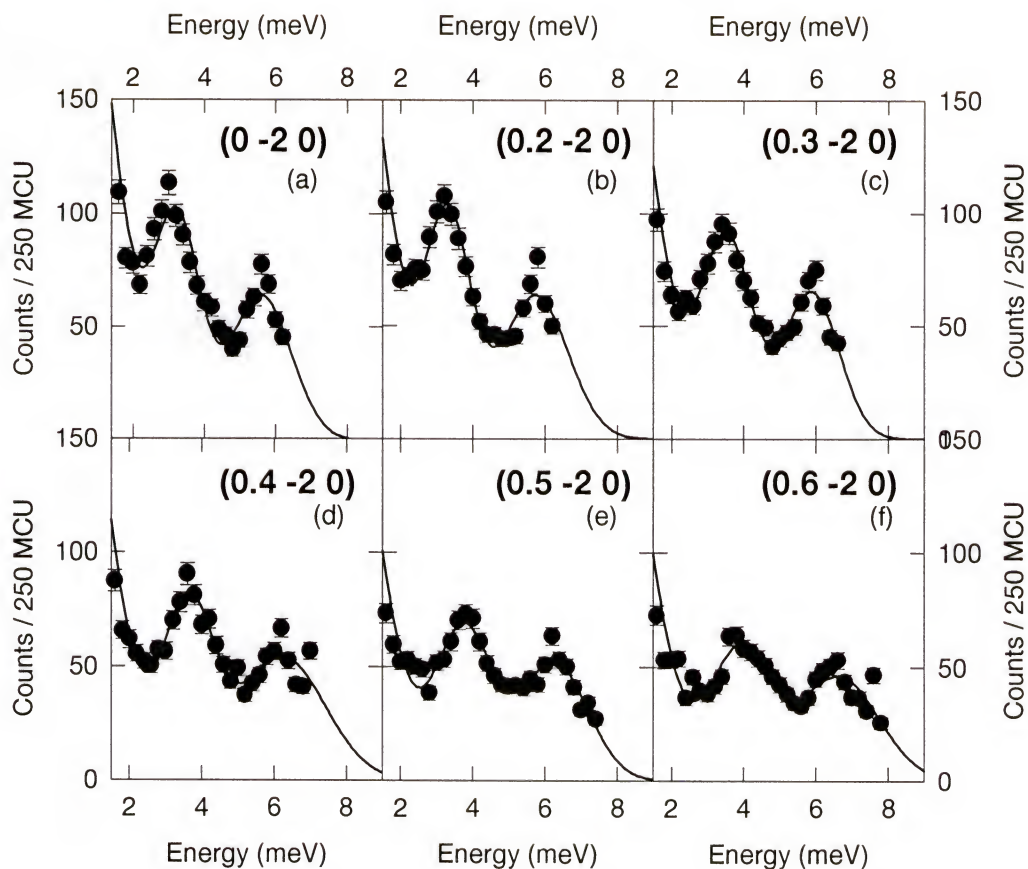


Figure 6-10 Constant Q Scans in the VOPO Crystal a^* Direction

A series of constant Q scans (a-f) of the VOPO crystal array, taken at the HB1A spectrometer with fixed $E_i = 14.7$ meV. The peak locations increase away from the zone edge at $(0 -2 0)$.

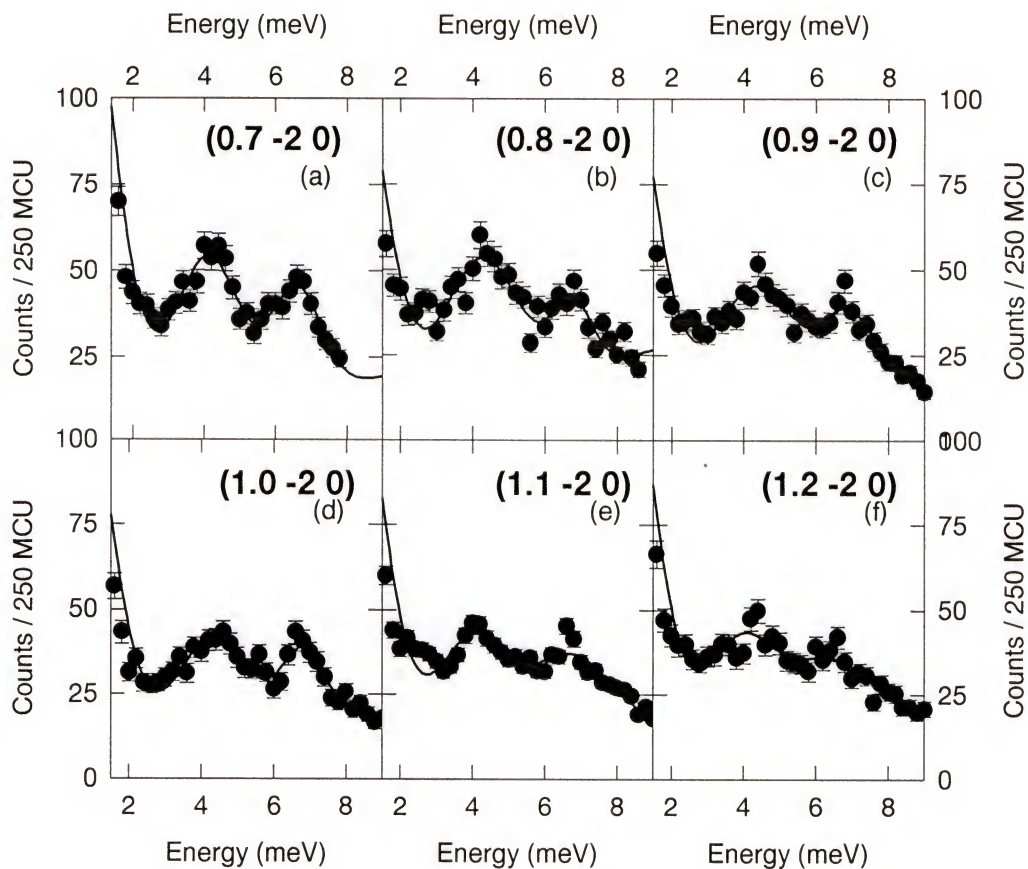


Figure 6-11 Constant Q Scans in the VOPO Crystal a^* Direction

A series of constant Q scans (a-f) of the VOPO crystal array, taken at the HB1A spectrometer with fixed $E_i = 14.7$ meV. The peak locations increase away from the zone edge at (0 -2 0).

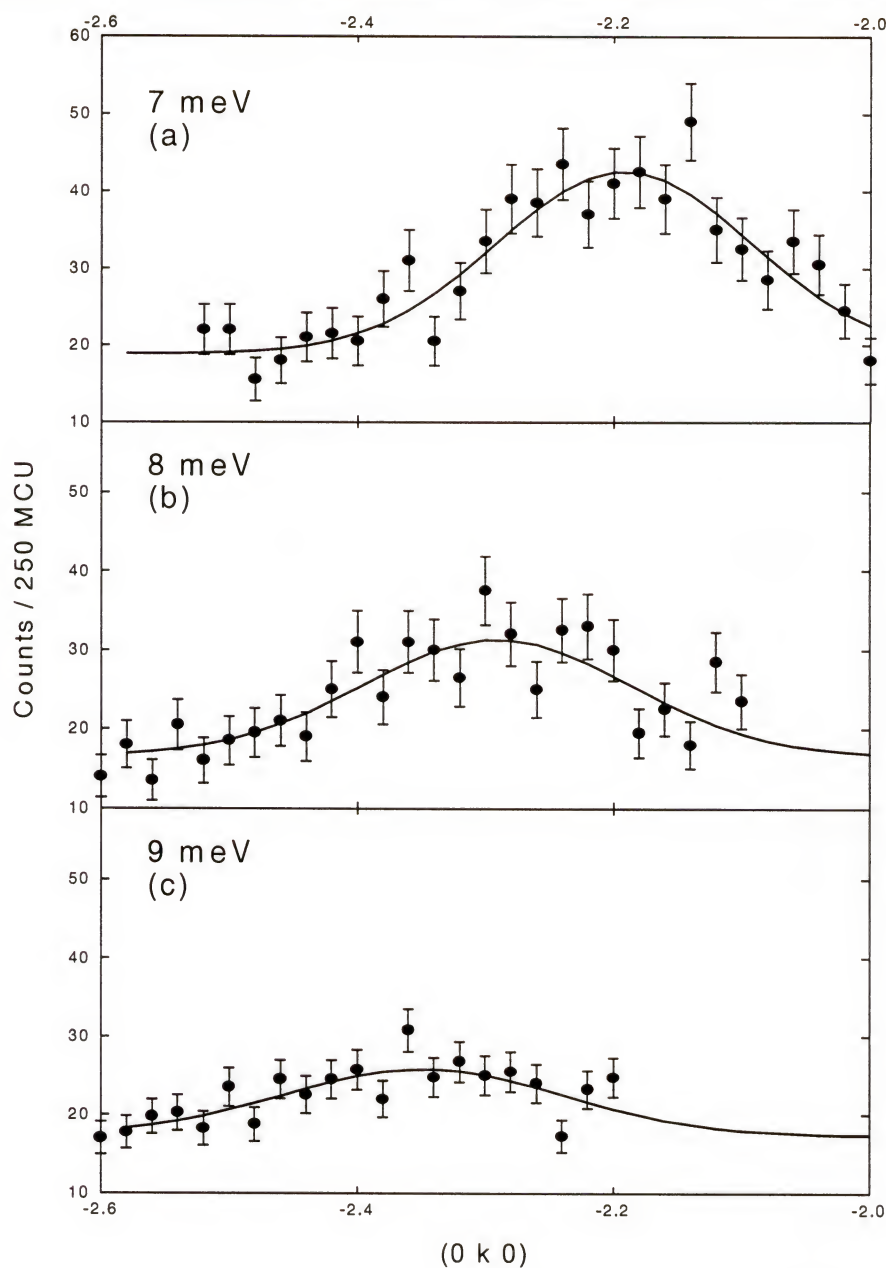


Figure 6-12 Constant Energy Scans of VOPO Array

A series of constant-E scans (a-c) of the VOPO crystal array from the HB3 spectrometer at 1.5K. The scans are taken in the $(0\ k\ 0)$ direction. Each panel covers a different range in Q , with cutoffs due to kinematic limitations. Each fit is done with a full resolution convolution.

6.2.5 High energy excitations

Two methods were used to gather dispersion data in the crystallographic $\vec{b}^*$ direction. The first was to take constant energy scans, changing the Q vector of the crystal. Three such scans are shown in Figure 6-12. In each case only a single peak is observed, instead of the two excitations observed in the constant- $\vec{Q}$ scans. This has two possible causes. Either the two peaks converge, or the resolution is simply too broad to observe the difference.

Constant energy scans proved insufficient to obtain the important zone boundary energy. However, constant- $\vec{Q}$ scans were also unable to observe the excitation energy at a $\vec{Q}$ of (0 -3 0) or (1 -3 0), as the excitation energy proved to be greater than what was achievable there due to kinematic limits. The zone boundary energy could be observed at (0 -5 0), and these scans are shown in Figure 6-13.

The scans shown in Figure 6-13 provide evidence for the location of the zone boundary in the crystal b^* direction, but they also show, at least, that the observed peak is magnetic. There are two methods that can be used to show that a peak is magnetic, and both were used. First, the temperature dependence of the peak may be used to indicate whether it is magnetic, as it should decrease with temperature. Second, the peak intensity will decrease with Q if the peak is magnetic.

Scans of the zone boundary at (0 -5 0) are shown in Figure 6-13(a) and (b), at 1.5K and 50K respectively. The difference between these two scans is the magnetic peak. Figure 6-14 shows the (0 -7 0) zone boundary, also at 1.5K and 50K. There is no observable difference between these two scans, which indicates that the intensity of the magnetic peak has decreased beyond observable levels. This decrease in intensity with $\vec{Q}$ provides further evidence that the peak in Figure 6-13(c) is magnetic in origin.

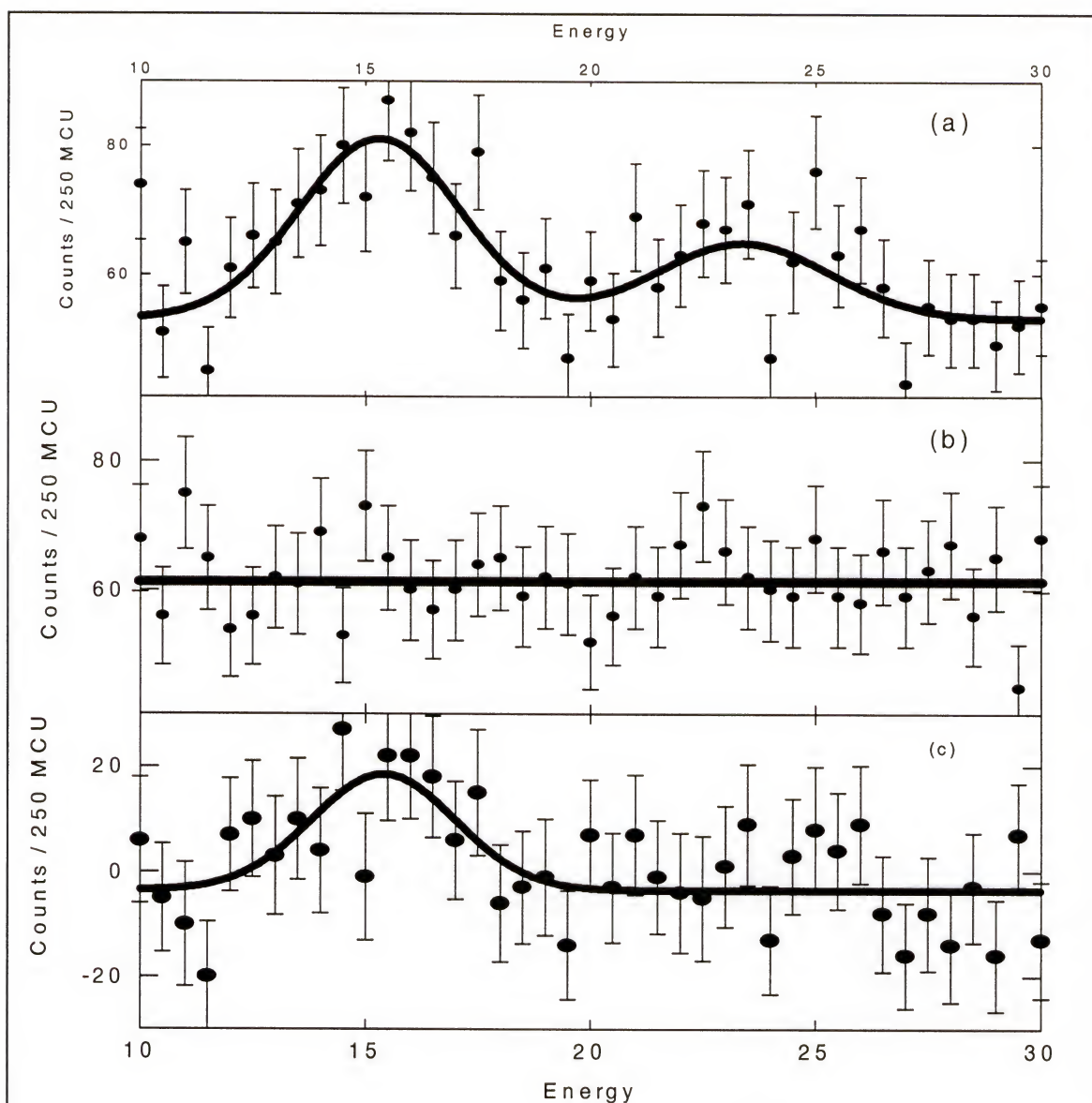


Figure 6-13 Zone Boundary of VOPO Array in b direction

Panel (a) shows a constant-Q scan at the (0 -5 0) peak taken at HB3 using a fixed final energy of 30.5 meV, at a temperature of 1.5K. Panel (b) is the same scan at 50 K. Panel (c) shows a point by point subtraction of the 50 K scan from the 1.5 K scan. All fits shown are simple gaussians with a constant background, in order to obtain the dispersion at the edge of the magnetic Brillouin Zone.

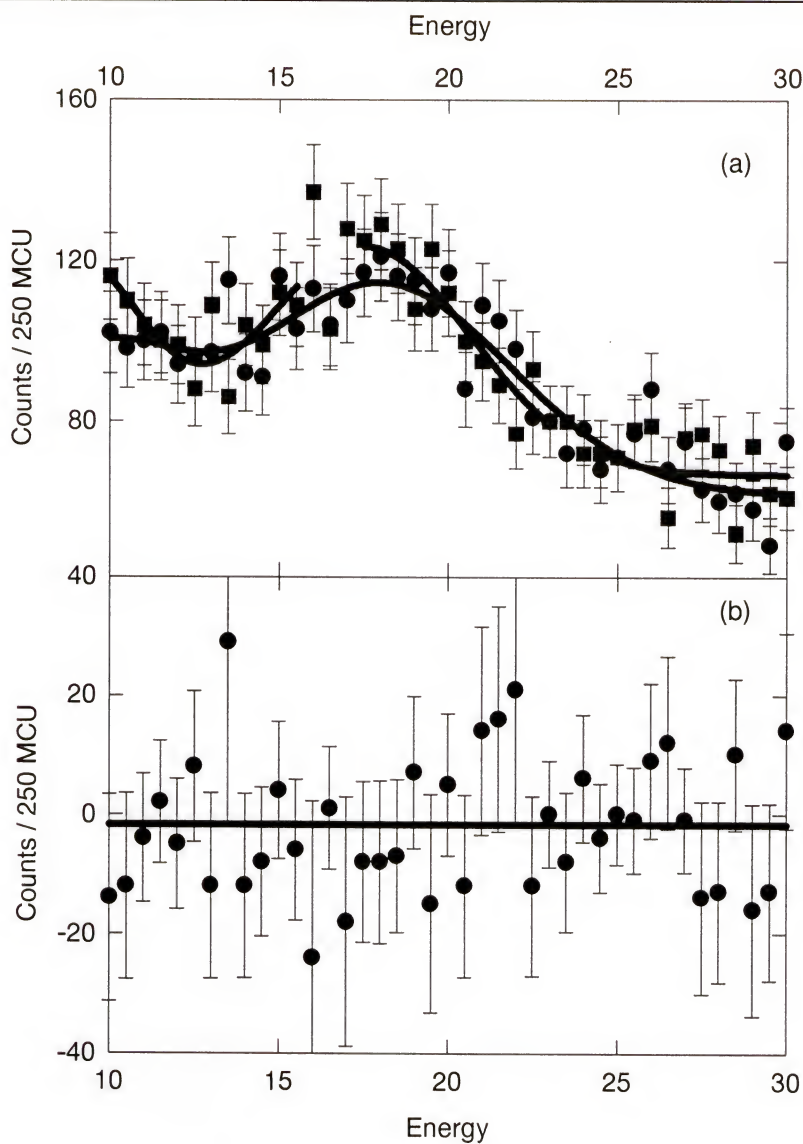


Figure 6-14 Constant Q Scan of the (0 -7 0) Zone Boundary

Scans of the (0 -7 0) zone boundary taken at the HB3 spectrometer with $E_f = 30.5$ meV.

Panel (a) shows scans taken at 1.5K and 50K, both fit by a sum of 2 gaussians with a constant background. Panel (b) shows the difference between these two scans, fit by a gaussian with a constant background, which represents the magnetic portion of the scattering.

Table 6-2 Model Fits to VOPO Dispersion

Model	J_0 or $J_{\parallel}$ (meV)	α_0 or $\epsilon_{\parallel}$	J_1 or $J_{\perp}$ (meV)	α_1 or $\epsilon_{\perp}$
Observed	12.5 (J_0)	0.89	9.9 (J_1)	0.87
Isotropic Chain	11.11 (J_0)	1	8.02 (J_1)	1
Spin Ladder	7.79 ($J_{\parallel}$)	1	7.79 ($J_{\perp}$)	1

6.3 Observed Dispersion Of $(VO)_2P_2O_7$ Crystal Array

A mixture of constant $\vec{Q}$ and constant E scans, as detailed in the Section 6.2, were used to determine the dispersion of the magnetic modes of VOPO. Two modes are evident through the entire dispersion curve in the crystal $\vec{a}^*$ and $\vec{c}^*$ directions, but it is unclear whether they remain separate or converge in the $\vec{b}^*$ direction. Section 6.3.1 begins by showing the dispersion in each of the three crystal directions, and then examines the implication of each of the three directions to the proposed models of magnetic exchange in Section 6.3.2.

6.3.1 Dispersion in each direction

The dispersion curves in each of the three directions are shown in Figure 6-15. The fits shown on the graphs are to the anisotropic chain. Ambiguity exists in the fit to the $\vec{b}$ direction. Two choices for the anisotropy lead to two possible solutions, one in which the two modes cross, and another where they do not. The non-crossing choice is displayed.

The parameters obtained in the fit displayed in Figure 6-15 are shown in Table 6-2. They are compared to the values reported previously for an isotropic alternating chain and a symmetric spin ladder.¹⁰

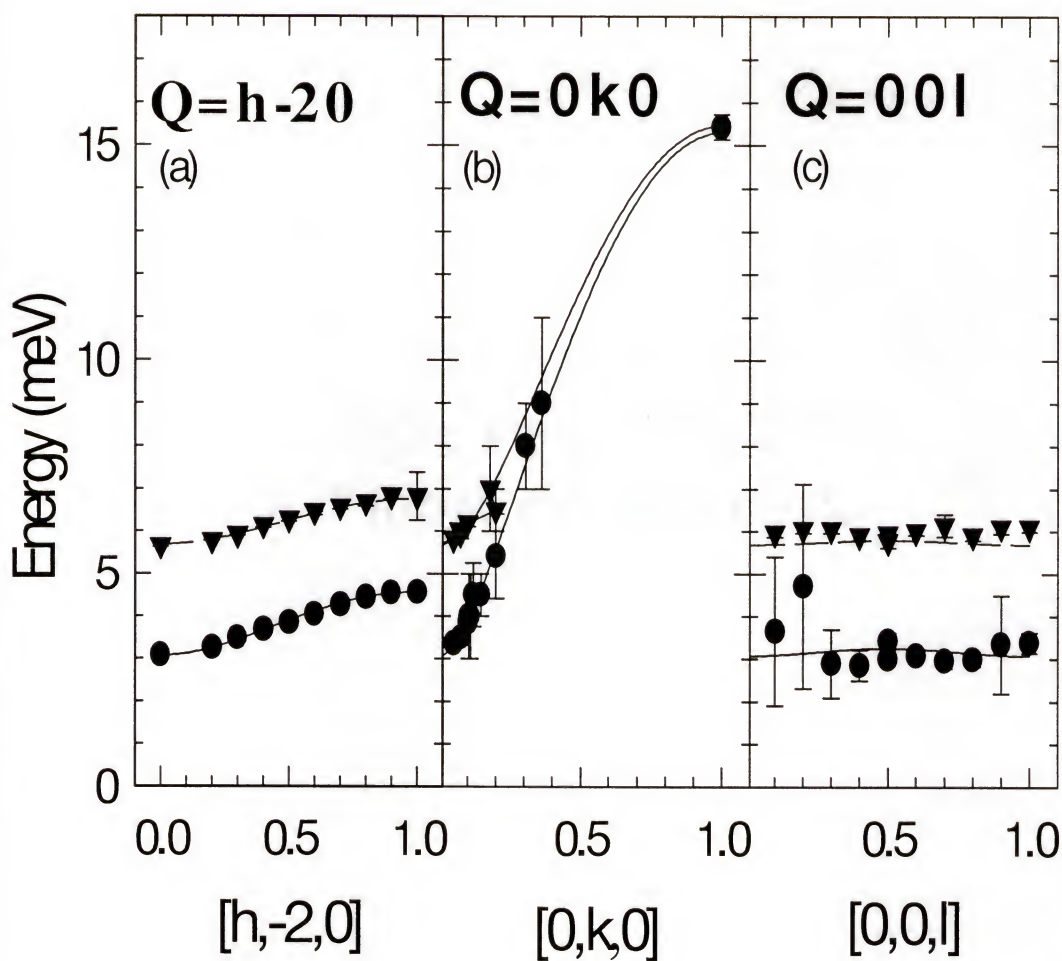


Figure 6-15 Dispersion of VOPO Magnetic Modes

The dispersion curves in each crystal direction for the VOPO array are shown in panels (a-c). The curves are obtained through a variety of methods, including constant-Q scans, constant-E scans, and scans in higher Brillouin Zones, all as described in the text.

6.3.2 Dispersion in crystal directions

The three dispersion curves shown in Figure 6-15 are each examined individually.

The implications for magnetic exchange are discussed.

6.3.2.1 Dispersion in the crystal $\vec{c}$ direction

There is no dispersion in the $\vec{c}$ direction. This is consistent with both the potential models for magnetic exchange in VOPO. Neither spin ladders nor alternating chains would give dispersion in this direction. This was the only dispersion curve not to provide any surprises.

6.3.2.2 Dispersion in the crystal $\vec{a}$ direction

One large surprise came from the ferromagnetic nature of the dispersion in the $\vec{a}$ direction. This is entirely inconsistent with the spin ladder model, and can be safely regarded as conclusive proof that VOPO is not a spin ladder.

The strength of this ferromagnetic interaction is weak, considerably smaller than the strength of the interaction in the $\vec{b}$ direction. The exchange path is through a single O atom, and single-exchange paths are normally antiferromagnetic. However, there is a strong Jahn-Teller distortion in the crystal $\vec{a}$ direction⁴⁰. The shorter leg of the path is 0.9Å, while it is 1.3Å in the longer leg. This argues for an unoccupied orbital in the vanadium d-orbital, with the occupied orbitals in the b-c plane. This under occupied orbital in the crystal $\vec{a}$ direction would give rise to a ferromagnetic interaction, which is what is observed.

6.3.2.3 Dispersion in the crystal $\vec{b}$ direction

The dispersion in the $\vec{b}$ direction is both strong and antiferromagnetic. While there are clearly two modes at the zone center, it is unclear whether there are still 2 modes at the boundary. If the origin of the two modes arises from anisotropy, the two modes will continue as separate modes, as shown in Equation (3–29).

If, as recent work suggests, there is a bound mode in an alternating chain⁵, the two modes may converge near the zone boundary. As of this writing, that question has not been resolved.

6.4 Conclusions

The experiments on the single crystal array of VOPO provide some definitive knowledge about the material, while still leaving some questions open. Specifically, they show conclusively that VOPO is not a spin ladder, while providing strong evidence that it is an alternating chain. The questions that remain open revolve around the origin of the second excitation, at 6 meV.

Section 6.4.1 begins by explaining why the spin ladder is ruled out by the observed dispersion. The exchange paths that lead to an alternating chain in the crystal $\vec{b}$ direction are examined in Section 6.4.2. Finally, the existence of the second excitation, not predicted in either the spin ladder or alternating chain model, is examined in Section 6.4.3.

6.4.1 Failure of the spin ladder model

The strongest evidence against the spin ladder model proposed for VOPO is the ferromagnetic interaction in the crystal $\vec{a}$ direction. The spin ladder model that had been proposed had antiferromagnetic exchange in both the $\vec{a}$ and $\vec{b}$ directions. The dispersion shown in Figure 6-15(a) is clearly ferromagnetic.

The structure of VOPO, as shown schematically in Figure 5-1, was used to determine the magnetic structure of the material.⁴⁰ This was in turn backed up by the magnetic susceptibility fit.¹⁰ However, as shown in Figure 3-6 and Figure 3-10, the magnetic susceptibility curves for spin ladders and alternating chains are so similar that they cannot be distinguished.

6.4.2 Magnetic exchange in the alternating chain model

The exchange paths for VOPO as an alternating chain are straightforward. The first exchange is the V-O-V path that was originally proposed as the spin ladder “rung.” This path has a length of 3.1 Å and has a single atom acting as an intermediary for the exchange. These are typical characteristics of an antiferromagnetic exchange.⁸⁸

The second exchange is the V-O-P-O-V exchange, shown schematically in Figure 5-1. This exchange length is $4.8\text{\AA}$, with three atoms carrying the exchange. These are highly atypical characteristics for a strong exchange. The same exchange is seen in the precursor material VODPO, though, and the structures are extremely similar. The biggest change in the magnetic properties of the materials appears to be the great strengthening of the V-O-V exchange, while the longer path remains of similar strength.

The final exchange is the weak ferromagnetic exchange in the crystal $\vec{a}$ direction. This is also a V-O-V exchange, over a Jahn-Teller distortion, which can explain why the exchange is both weak and ferromagnetic.

6.4.3 Potential explanations of the second excitation

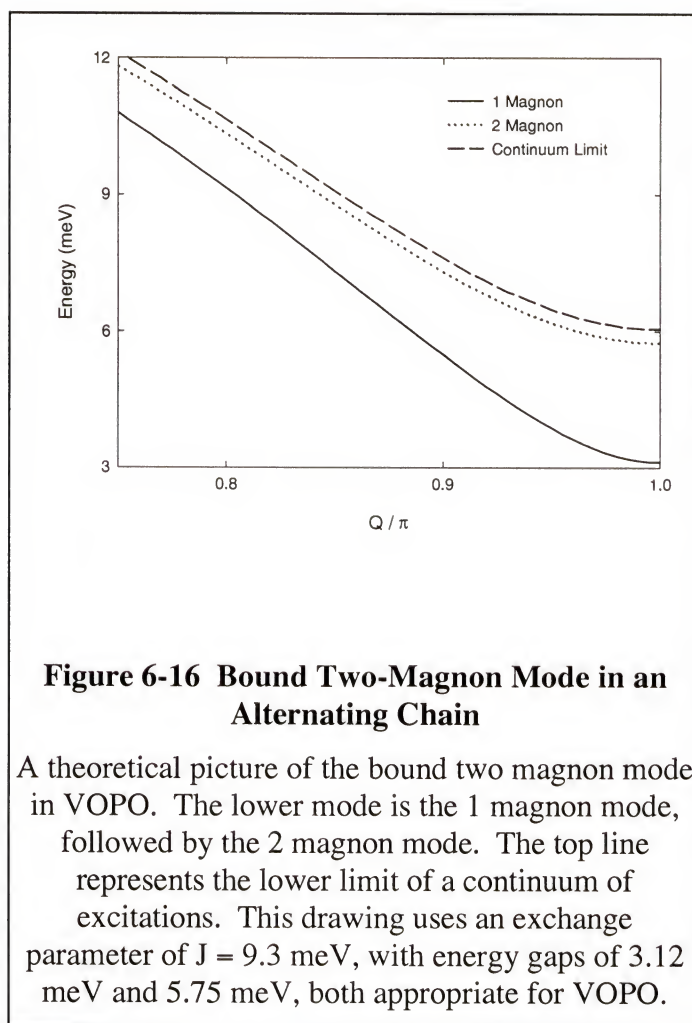
The alternating chain model fits the observed data on VOPO on its structure, magnetic susceptibility, and its dispersion, except for one detail. The alternating chain model presented in Chapter 3 predicts a single mode, while two excitations are observed. This is an important detail, and two potential explanations are presented below.

6.4.3.1 Spin anisotropy

The first, and perhaps simplest, explanation, is that the alternating chain is anisotropic. This would split the first excited mode in two. The first mode in the isotropic chain is a triplet, and would split into an $S_z = 0$ singlet and an $S_z = \pm 1$ doublet. The magnitude of the split is determined by the anisotropy.

An anisotropic alternating chain would have its dispersion split into two modes at all points in the Brillouin Zone. While only a single mode is observed at the zone boundary, that is inconclusive. The resolution at that point was insufficient to determine whether one or two modes were present.

There are two strong arguments against anisotropy. The VODPO excitation did not show any evidence of spin anisotropy. The structural changes between VODPO and



VOPO do not give rise to any expectation that anisotropy should develop. The g-factor of the V^{4+} ion is close to 2, indicative of isotropy, in many other vanadium phosphates.¹⁰²

The magnetic susceptibility also provides evidence that anisotropy is not present. The powder magnetic susceptibility is best fit by an isotropic chain. The fit to the susceptibility by a spin ladder is also isotropic.

6.4.3.2 Alternating chain

Another explanation for the second mode is a bound mode. Recent work⁵ has indicated a possible bound excitation in alternating chains with sufficiently large alternation parameters. It has been shown for an isotropic alternating chain, the energy

gap Δ depends on the alternation parameter, defined by Uhrig and Shultz as $\delta = (\beta - 1)/(\beta + 1)$, where $\beta = J_0/J_1$. The limit $\delta = 0$ is equivalent to the spin chain limit, and is gapless.

For $\delta > 0$ a gap opens, and the lowest excitation is a well defined $S=1$ triplet mode. For small δ a second gap to the original continuum of the spin chain is expected at an energy of 2Δ . The theory predicts that for $\delta > 0.08$, a second sharp triplet mode will appear at energies just below the continuum. If the exchange in VOPO is assumed to be isotropic, the alternation parameter would be $\delta \approx 0.1$. It is plausible that the observed second mode is this two-magnon bound state.

A theoretical picture of the two magnon picture is shown in Figure 6-16. The numbers used to create this graph are appropriate to those found from the VOPO data. It must be noted that, while the two bound modes are similar to the observed excitations, no trace of a continuum was observed.

CHAPTER 7

CONCLUSIONS

The work presented in this thesis proves that the magnetic structure of VOPO is best represented as an alternating chain, and that it is not a spin ladder at all. The dispersion from the single crystal array, shown in Figure 6-15 is alone sufficient to discredit the spin ladder theory. The strong dispersion in the crystal $\vec{b}^*$ direction is well fit by the anisotropic alternating chain model presented in the text.

Additional insight into the nature of the magnetic exchange was presented by examining the precursor material VODPO. This magnetic dimer was found to exhibit strong exchange over a long distance due to a “covalent bridge” formed by a phosphate group. This phosphate bridge becomes the proposed separation between ladders when VODPO transforms to become VOPO. Allowing that exchange to remain strong in VOPO, along with a weak interaction in the crystal $\vec{a}^*$ direction (see Figure 6-15) leads naturally to an alternating chain description of magnetic exchange.

Two important questions about the magnetic exchange in VOPO remain unanswered. The first and most important is the origin of the second excitation shown in the dispersion. The fits shown in this thesis assume spin anisotropy is the cause, but the experimental evidence is insufficient to prove that. Arguments against that case have also been presented. This question can be resolved by examining the crystal in a magnetic field. The field would split excitations with $S_z \neq 0$. So, if the excitation is caused by anisotropy, one of the two excitations would split into two excitations, while the other excitation would remain unaffected. If the two excitations are both bound modes, then both excitations would be spin-1 triplets, and would be split into three excitations by the

application of a field. The crystal array used in the experiments described in this thesis has too great a mosaic spread to be used effectively in this experiment.

The second question concerns the exchange along the crystal $\vec{a}^*$ direction, which is weakly ferromagnetic. The proposed exchange path was a simple V-O-V, with ferromagnetic exchange caused solely by the distortion of the VO_6 octahedra. To determine the exchange would require a calculation of the full structure factor as well as careful measurements of the integrated intensities of the excitations. Again, the crystal array used in this thesis is inappropriate for this experiment, due to the large mosaic and difficulties in measurements off principal axes.

The results presented have also indicated the need for more theoretical work on both the alternating chain and spin ladder Hamiltonians. The success of the pseudo-boson approximation in predicting the lowest level excitation demands further investigation. Additional terms, representing two-magnon and three-magnon excitations, can be included in the expansion. This treatment should emphasize the search for additional bound modes.

In sum, low-dimensional magnetic systems may prove a rich area for additional research. Their simple Hamiltonians admit detailed solutions, with complex and subtle behavior.

REFERENCES

- 1 F.D.M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983).
- 2 M. Nishi, O. Fujita, and J. Akimitsu, Phys. Rev. B **50**, 6508 (1994).
- 3 S.A. Carter, B. Batlogg, R.J. Cava, J.J. Krajewski, W.F. Peck, Jr., and T.M. Rice, Phys. Rev. Lett. **77**, 1378 (1996).
- 4 E. Dagatto and T.M. Rice, Science **271**, 618 (1996).
- 5 G.S. Uhrig and H.J. Schulz, Phys. Rev. B **54**, R9624 (1996).
- 6 E. Dagatto and A. Moreo, Phys. Rev. B **38**, 5087 (1988).
- 7 R.M. Morra, W.J.L. Buyers, R.L. Armstrong and K. Hirakawa, Phys. Rev. B **38**, 543 (1988).
- 8 D.C. Johnston and J.W. Johnson, J. Chem. Soc. Chem. Commun. **1985**, 1720 (1985).
- 9 D. Beltrán-Porter, P. Amorós, R. Ibáñez, E. Martínez, A. Beltrán-Porter, A. Le Bail, G. Ferey, and G. Villeneuve. Solid State Ionics **32/33**, (1989) 57.
- 10 T. Barnes and J. Riera, Phys. Rev. B **50**, 6817 (1994).
- 11 R.S. Eccleston, T. Barnes, J. Brody, and J.W. Johnson, Phys. Rev. Lett. **73**, 2626 (1994).
- 12 A.W. Garrett, S.E. Nagler, T. Barnes and B.C. Sales, Phys. Rev. B **55**, 3631 (1997).
- 13 A.W. Garrett, S.E. Nagler, D.A. Tennant, B.C. Sales and T. Barnes, Phys. Rev. Lett. **79**, 745 (1997).
- 14 D.A. Tennant, S.E. Nagler, A.W. Garrett, T. Barnes and C.C. Torardi, Phys. Rev. Lett. **78**, 4998 (1997).
- 15 S.W. Lovesey, Theory of Neutron Scattering from Condensed Matter, (Oxford University Press, New York, 1984).
- 16 S.V. Vonsovskii, Magnetism, (Halsted Press, New York, 1974).
- 17 R. Celotta and J. Levine, Neutron Scattering, (Academic Press, Orlando, 1986).
- 18 Y.A. Izyumov, R.P. Ozerov, Magnetic Neutron Diffraction, (Plenum Press, New York, 1970).
- 19 G.L. Squires, Introduction to the theory of Thermal Neutron Scattering, (Cambridge University Press, Cambridge UK).

- 20 Neutron Scattering at the High Flux Isotope Reactor, (Martin Marietta Energy Systems, Inc., 1990).
- 21 C. Kittel, Introduction to Solid State Physics, (John Wiley & Sons Inc., New York 1953).
- 22 W. Heisenberg, Z. Physik 49, 619 (1928).
- 23 P.W. Anderson, Phys. Rev. 79 350 (1950).
- 24 L. Néel, Ann. Physique 17, 5 (1932).
- 25 H.A. Bethe, Z. Physik 71, 205 (1931).
- 26 P.W. Anderson, Phys. Rev. 86, 694 (1952).
- 27 S. Tomonaga, Prog. Theor. Phys. (Kyoto) 5, 544 (1950).
- 28 R. Shankar, Principles of Quantum Mechanics, (Plenum Press, New York, 1987).
- 29 J.W. Bray, L.V. Interrant, I.S. Jacobs, and J.C. Bonner, in Extended Linear Chain Compounds, ed. J.S. Miller, (Plenum, New York, 1983) Vol. 3 pp. 353-415.
- 30 L.W. ter Haar, and W.E. Hatfield, Inorg. Chem. 24, 1022 (1985).
- 31 B. Leuenberger, A. Stebler, H.P.U. Güdel, A. Furrer, R. Feik, and J.K. Kjems, Phys. Rev. B 30, 6300 (1984).
- 32 M.T. Hutchings, G. Shirane, R.J. Birgeneau, and S.L. Holt, Phys. Rev. B 5, 1999 (1972).
- 33 Y. Endoh, G. Shirane, R.J. Birgeneau, P.M. Richards, and S.L. Holt, Phys. Rev. Lett. 32, 170 (1974).
- 34 I.U. Heilmann, G. Shirane, Y. Endoh, R.J. Birgeneau, and S.L. Holt, Phys. Rev. B 18, 3530 (1978).
- 35 M.T. Hutchings, H. Ikeda, and J.M. Milne, J. Phys. C 12, L739 (1979).
- 36 S.K. Satija, J.D. Axe, G. Shirane, H. Yoshizawa, and K. Hirakawa, Phys. Rev. B 21, 2001 (1980).
- 37 M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett 70, 3651 (1993).
- 38 R.S. Eccleston, M. Azuma, and M. Takano, Phys Rev. B 53, R14721 (1996).
- 39 M. Takano, Z. Hiroi, M. Azuma, and Y. Takeda, Jap. J. of Appl. Phys. Series 7, 3 (1992).
- 40 D.C. Johnston, J.W. Johnson, D.P. Goshorn, and A.J. Jacobson, Phys. Rev. B 35, 219 (1987)
- 41 J. des Cloizeaux and J.J. Pearson, Phys. Rev. 128, 2131 (1962).
- 42 J.C. Bonner and H.W.J. Blöte, Phys. Rev. B 25, 6959 (1982).
- 43 S.R. White, R.M. Noack, and D.J. Scalapino, Phys. Rev. Lett. 73, 886 (1994).

- 44 A.B. Harris, Phys. Rev. B 7, 3166 (1973).
- 45 T. Barnes, E. Dagatto, J. Riera, and E.S. Swanson, Phys. Rev. B 44, 3196 (1993).
- 46 E. Dagotto, and A. Moreo, Phys. Rev. B 38, 5087 (1988).
- 47 E. Dagotto, and A. Moreo, Phys. Rev. B 44, 5396 (1991).
- 48 E. Dagotto, J. Riera, and D. Scalapino, Phys. Rev. B 45, 5744 (1992).
- 49 S.P. Strong, and A.J. Millis, Phys. Rev. Lett. 69, 2419 (1992).
- 50 T. Barnes, E. Dagotto, J. Riera, and E.S. Swanson, Phys. Rev. B 47, 3196 (1993).
- 51 M. Greven, Z. Phys. B 96, 465 (1995).
- 52 J.C. Bonner, S.A. Friedberg, H. Kobayashi, D.L. Meier, and H.W.J. Blöte, Phys. Rev. B 27, 248 (1983).
- 53 W.E. Hatfield, J. Appl. Phys. 52, 1985 (1981).
- 54 Z. Hiroi, M. Azuma, M. Takano, and Y. Bando, J. Solid State Chem. 95, 230 (1991).
- 55 B. Batlogg, Bull. Am. Phys. Soc. 40, 327 (1995).
- 56 G. Chaboussant, P.A. Crowell, L.P. Lévy, O. Piovesana, A. Madouri, and D. Mailly, Phys. Rev. B 55, 3046 (1997).
- 57 D.G. Shelton, A.A. Nersesyan, and A.M. Tsvelik, Phys. Rev. B 53, 8521 (1996).
- 58 M. Greven, R.J. Birgeneau, and U.J. Wiese, Phys. Rev. Lett. 77, 1865 (1996).
- 59 H.Q. Lin, Phys. Rev. B 42, 6561 (1990).
- 60 C. Lanczöz, J. Res. Natl. Bur. Stand. 45, 255 (1950).
- 61 J. Eckert, D.E. Cox, G. Shirane, S.A. Friedberg, and H. Kobayashi, Phys. Rev. B 20, 4596 (1979).
- 62 J.C. Bonner, S.A. Friedberg, H. Kobayashi, and B.E. Myers, in Proceedings of the 12th International Conference on Low Temperature Physics, Kyoto, Japan 1970, ed. E. Kanda (Keigaku, Tokyo, 1971).
- 63 K.M. Diederix, W.H.J. Blöte, J.P. Groen, J.O. Klaassen, and N.J. Poulis, Phys. Rev. B 19, 420 (1979).
- 64 C.C. Torardi and J.C. Calabrese, Inorg. Chem. 23, (1984) 1308.
- 65 C.C. Torardi, Z.G. Li, H.S. Horowitz, W. Liang, and M.H. Whangbo, J. Solid State Chem. 75, 2003 (1994).
- 66 H.S. Horowitz, C.M. Blackstone, A.W. Sleight, and G. Jeuffer, Appl. Catal. 38, 193 (1988).
- 67 G. Centi, F. Trifiro, and G. Poli, Appl. Catal. 19, 225 (1985).
- 68 M.E. Lenowicz, J.W. Johnson, J.F. Brody, H.F. Shannon, Jr., and J.M. Newsom, J. Solid State Chem. 56 370 (1985).

- 69 G. Busca, F. Cavani, G. Centi, and F. Trifero, *J. Catal.* 90, 400 (1986).
- 70 E. Bordes, P. Courtine, and J.W. Johnson, *J. Solid State Chem.* 55, 270 (1984).
- 71 J.W. Johnson, D.C. Johnston, A.J. Jacobson, and F.J. Brody, *J. Am. Chem. Soc.* 106, 8123 (1984).
- 72 P. Amorós, R. Ibáñez, A. Beltrán, D. Beltrán, A. Fuertes, P. Gomez-Romero, E. Hernandez, and J. Rodriguez-Carvajal, *Chem. Mater.* 3, 407 (1991).
- 73 D. Beltrán-Porter, P. Amorós, R. Ibáñez, E. Martínez, A. Beltrán-Porter, A. Le Bail, G. Ferey, and G. Villeneuve. *Solid State Ionics* 32/33, (1989) 57.
- 74 D. Papoutsakis, J.E. Jackson, and D.G. Nocera. *Inorg. Chem.* 35, (1996) 800.
- 75 M.E. Leonowicz, J.W. Johnson, J.F. Brody, H.F. Shanson, and J.M. Newsam, *J. Solid State Chem.* 56 (1985) 370.
- 76 J.W. Johnson, D.C. Johnston, D.P. Goshorn, and A.J. Jacobson, *Phys. Rev. B* 35, 219 (1987).
- 77 D. Papoutsakis, J.E. Jackson, and D.G. Nocera, *Inorg. Chem.* 35, 800 (1996).
- 78 K.H. Lii, *Chin. Chem. Soc.* 39, 569 (1992).
- 79 S.L. Wang, H.Y. Kang, C.Y. Cheng, and K.H. Lii, *Inorg. Chem.* 30, 3496 (1991).
- 80 H.Y. Kang, W.C. Lee, S.L. Wang, and K.H. Lii, *Inorg. Chem.* 31, 4743 (1991).
- 81 M. Popovicic, *Acta Crystallographica A*, 31 (1975).
- 82 J.H. Hicks, *Neutron Scattering*, (Academic Press, New York, 1979).
- 83 P. Brüesch, *Phonons: Theory and Experiments I, Solid-State Sciences*, (Springer-Verlag, Heidelberg, 1982), Vol. 34.
- 84 A. Furrer, and H.U. Güdel, *Phys. Rev. Lett.* 39, 657 (1977).
- 85 M.A. Aebersold, H.U. Güdel, A. Hauser, A. Furrer, H. Blank, and R. Kahn, *Phys. Rev. B* 48, 12723 (1993).
- 86 A. Zheludev, G. Shirane, Y. Sasago, M. Hase, and K. Uchinokura, *Phys. Rev. B* 53, 17642 (1996).
- 87 P.J. Brown, in *International Tables for Crystallography*, (Kluwer Academic Press, London, 1992), Vol. 3.
- 88 J.B. Goodenough, *Magnetism and the Chemical Bond*, (Interscience, J. Wiley and Sons, London, 1963).
- 89 B. Lake, D.A. Tennant, R.A. Cowley, J.D. Axe, and C.K. Chen, *J. Phys. Cond. Mat.* 8, 8613 (1996).
- 90 C.C. Torardi, J.C. Calabrese, K. Lázár, and W.M. Reiff, *J. Solid State Chem.* 51, 376 (1984).

- 91 M. Azuma, Z. Hiroi, M. Takano, K. Ishida, and Y. Kitaoka, Phys. Rev. Lett. 73, 3463 (1994).
- 92 Y. Gorbunova and S.A. Linde, Dokl. Akad. Nauk SSSR 245, 584 (1979).
- 93 S.A. Linde, Y.E. Gorbunova, A.V. Lavrov, and Y.G. Kustnetsov, Dokl. Akad. Nauk SSSR 224, 1411 (1979).
- 94 P. T. Nguyen, R. D. Hoffman, and A. W. Sleight, Mat. Res. Bull. 30, 9, 1055 (1995).
- 95 R.M. Noack, S.R. White, and D.J. Scalapino, Phys. Rev. Lett. 73, 882 (1994).
- 96 S. Gopalan, T.M. Rice, and M. Sigrist, Phys. Rev. B 49, 8901 (1994).
- 97 M. Sigrist, T.M. Rice, and F.C. Zhang, Phys. Rev. B 49, 12058 (1994).
- 98 H. Tsunetsugu, M. Troyer, and T.M. Rice, Phys. Rev. B 49 16078 (1994).
- 99 D. Poilblanc, H. Tsunetsugu, and T.M. Rice, Phys. Rev. B 50, 6511 (1994).
- 100 M. Azzouz, L. Chen, and S. Moukouri, Phys. Rev. B 50, 6233 (1994).
- 101 R.R. Joyce and P.L. Richards, Phys. Rev. 179, 375 (1969).
- 102 D. Ballutard, E. Bordes, and P. Courtine, Mater. Res. Bull. 17, 519 (1982).

APPENDIX A

CALCULATION OF THE DISPERSION OF AN ALTERNATING CHAIN AND SPIN LADDER USING PSEUDO-BOSON OPERATORS

The dispersion of the alternating chain and spin ladder Hamiltonians was quoted in Chapter 3 of the text. The derivation is presented in this appendix. The two calculations are similar in many ways, and so are presented together, in both cases for an anisotropic case. The isotropic case can easily be obtained from the anisotropic solution by setting the anisotropic elements to 1.

A.1 Transforming Hamiltonians into Pseudo-Boson Representation

The Hamiltonians for the alternating chain and spin ladder systems must be transformed into the pseudo-dimer representation before solving. This involves replacing the spin operators in the original Hamiltonian with creation and annihilation operators suitable for bosons - appropriate for a spin-1 dimer. This approximation allows local fluctuations for a spin-1 system, but introduces long range order into the system.

The original Hamiltonian for an alternating chain system is

$$\begin{aligned} \hat{H} = \sum_l J_0 \left[S_1^z(l) S_2^z(l) + \frac{\alpha_0}{2} (S_1^+(l) S_2^-(l) + S_1^-(l) S_2^+(l)) \right] \\ + J_1 \left[S_2^z(l) S_1^z(l+1) + \frac{\alpha_1}{2} (S_2^+(l) S_1^-(l+1) + S_2^-(l) S_1^+(l+1)) \right] \end{aligned} \quad (A-1)$$

where J_0 and J_1 are the exchange coefficients, and $J_0 > J_1$. α_0 and α_1 are the anisotropies of the two exchanges, and S_1 and S_2 are the two spins involved in the J_0 exchange.

The Hamiltonian for the spin ladder is similar,

$$\begin{aligned}
\hat{H} = & \sum_l J_{\perp} \left(S_1^z(l) S_2^z(l) + \frac{\epsilon_0}{2} (S_1^+(l) S_2^-(l) + S_1^-(l) S_2^+(l)) \right) \\
& + J_{\parallel} \left(S_1^z(l) S_1^z(l+1) + \frac{\epsilon_1}{2} (S_1^+(l) S_1^-(l+1) + S_1^-(l) S_1^+(l+1)) \right) \\
& + J_{\parallel} \left(S_2^z(l) S_2^z(l+1) + \frac{\epsilon_1}{2} (S_2^+(l) S_2^-(l+1) + S_2^-(l) S_2^+(l+1)) \right)
\end{aligned} \tag{A-2}$$

where S_1 and S_2 are a “rung” of the spin ladder, coupled by the exchange $J_{\perp}$. The position l counts along the “chain” direction of the ladder. Finally, ϵ_0 and ϵ_1 are the anisotropies in the rung and chain directions, respectively.

The same pseudo-boson operators will be used for both systems. The dimer has 4 states,

$$\begin{aligned}
|G\rangle &= \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \\
|\bar{1}\rangle &= |\downarrow\downarrow\rangle \\
|0\rangle &= \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\
|1\rangle &= |\uparrow\uparrow\rangle
\end{aligned} \tag{A-3}$$

where G is the spin-0 ground state. The other three states are all spin-1, with $S_z = -1, 0$, and $+1$ respectively. The pseudo-boson operators introduced are then

$$\begin{aligned}
a_0^\dagger |G\rangle &= |0\rangle & a_0 |0\rangle &= |G\rangle \\
a_1^\dagger |G\rangle &= |\bar{1}\rangle & a_1 |\bar{1}\rangle &= |G\rangle \\
a_1^\dagger |G\rangle &= |1\rangle & a_1 |1\rangle &= |G\rangle
\end{aligned} \tag{A-4}$$

which defines all the possible interactions.

It is possible to write the spin operators in terms of these pseudo-boson operators. Specifically,

$$\begin{aligned}
S_1^z &= \frac{1}{2}(a_0^\dagger + a_0) - \frac{1}{2}(a_1^\dagger a_1 - a_1^\dagger a_1) & S_2^z &= -\frac{1}{2}(a_0^\dagger + a_0) - \frac{1}{2}(a_1^\dagger a_1 - a_1^\dagger a_1) \\
S_1^+ &= -\frac{1}{\sqrt{2}}(a_1^\dagger - a_1) + \frac{1}{\sqrt{2}}(a_0^\dagger a_1 + a_1^\dagger a_0) & S_2^+ &= \frac{1}{\sqrt{2}}(a_1^\dagger - a_1) + \frac{1}{\sqrt{2}}(a_0^\dagger a_1 + a_1^\dagger a_0) \\
S_1^- &= \frac{1}{\sqrt{2}}(a_1^\dagger - a_1) + \frac{1}{\sqrt{2}}(a_0^\dagger a_1 + a_1^\dagger a_0) & S_2^- &= -\frac{1}{\sqrt{2}}(a_1^\dagger - a_1) + \frac{1}{\sqrt{2}}(a_0^\dagger a_1 + a_1^\dagger a_0)
\end{aligned} \tag{A-5}$$

These substitutions will only be performed on the perturbation.

Terms containing two of the pseudo-boson operators represent scattering from a single magnon, and may be presumed to dominate scattering. Only those terms will be retained in the following approximations.

In terms of the pseudo-boson approximation, the alternating chain Hamiltonian becomes

$$\begin{aligned}
\hat{H}_0 &= \sum_l \alpha_0 J_0 a_0^\dagger(l) a_0(l) + \frac{J_0(1+\alpha_0)}{2} (a_1^\dagger(l) a_1(l) + a_1^\dagger(l) a_1(l)) \\
\hat{H}_1^{BL} &= -\frac{J_1}{4} \sum_l (a_0^\dagger(l) + a_0(l)) (a_0^\dagger(l+1) + a_0(l+1)) \\
\hat{H}_1^{BT} &= \frac{J_1 \alpha_1}{4} \sum_l (a_1^\dagger(l) - a_1(l)) (a_1^\dagger(l+1) - a_1(l+1)) \\
&\quad + (a_1^\dagger(l) - a_1(l)) (a_1^\dagger(l+1) - a_1(l+1))
\end{aligned} \tag{A-6}$$

where the perturbation is divided into a longitudinal term, containing only a_0 terms, and a transverse term, containing no a_0 terms. The same substitution can be performed on the spin ladder Hamiltonian, resulting in

$$\begin{aligned}
\hat{H}_0 &= \sum_l \varepsilon_0 J_{\perp} a_0^{\dagger}(l) a_0(l) + \frac{J_{\perp}(1+\varepsilon_0)}{2} (a_1^{\dagger}(l) a_1(l) + a_1^{\dagger}(l) a_1(l)) \\
\hat{H}_1^{BL} &= \frac{J_{\parallel}}{2} \sum_l (a_0^{\dagger}(l) + a_0(l)) (a_0^{\dagger}(l+1) + a_0(l+1)) \\
\hat{H}_1^{BT} &= -\frac{J_{\parallel} \varepsilon_1}{2} \sum_l (a_1^{\dagger}(l) - a_1(l)) (a_1^{\dagger}(l+1) - a_1(l+1)) \\
&\quad + (a_1^{\dagger}(l) - a_1(l)) (a_1^{\dagger}(l+1) - a_1(l+1))
\end{aligned} \tag{A-7}$$

where the same breakdown is performed for the perturbations.

These approximations can be put into a more usable form by fourier transforming them. For the alternating chain, this results in

$$\begin{aligned}
\hat{H}^{BL} &= \sum_k \left(\alpha_0 J_0 - \frac{J_1}{2} \cos(kD) \right) a_k^{\dagger} a_{-k} - \frac{J_1}{4} \cos(kD) (a_k^{\dagger} a_{-k}^{\dagger} + a_k a_{-k}) \\
\hat{H}^{BT} &= \sum_k \left(\frac{J_0(1+\alpha_0)}{2} - \frac{J_1 \alpha_1}{2} \cos(kD) \right) (a_{-k1}^{\dagger} a_{k1}^{\dagger} + a_{k1}^{\dagger} a_{-k1}) \\
&\quad + \frac{J_1 \alpha_1}{2} \cos(kD) (a_{k1}^{\dagger} a_{-k1}^{\dagger} + a_{k1} a_{-k1})
\end{aligned} \tag{A-8}$$

where the original and perturbation Hamiltonians have been combined. D is the separation between two identical dimer positions. a_k is the Fourier transform of a_0 , while a_{k1} and $a_{k1}^{\dagger}$ are the transforms of a_1 and $a_1^{\dagger}$ respectively.

In the same fashion, the spin ladder Hamiltonian can be transformed to

$$\begin{aligned}
\hat{H}^{BL} &= \sum_k \left(\varepsilon_0 J_{\perp} + J_{\parallel} \cos(kd) \right) a_k^{\dagger} a_{-k} - \frac{J_{\parallel}}{2} \cos(kd) (a_k^{\dagger} a_{-k}^{\dagger} + a_k a_{-k}) \\
\hat{H}^{BT} &= \sum_k \left(\frac{J_{\perp}(1+\varepsilon_0)}{2} + J_{\parallel} \varepsilon_1 \cos(kd) \right) (a_{-k1}^{\dagger} a_{k1}^{\dagger} + a_{k1}^{\dagger} a_{-k1}) \\
&\quad - J_{\parallel} \varepsilon_1 \cos(kd) (a_{k1}^{\dagger} a_{-k1}^{\dagger} + a_{k1} a_{-k1})
\end{aligned} \tag{A-9}$$

where d is the separation of a rung dimer. All other terms are as defined in previous steps.

A.2 Solution of Transformed Hamiltonians

The two systems, alternating chain and spin dimer, have Hamiltonians that are similar in form, and so can be solved in similar fashions. The longitudinal and transverse modes have different forms, and so they will be separately.

Both of the longitudinal Hamiltonians, shown in Equations (A-8) and (A-9), each have the form

$$\hat{H} = \sum_k A_k a_k^\dagger a_{-k} + \frac{B_k}{2} (a_k^\dagger a_{-k}^\dagger + a_k a_{-k}) \quad (\text{A-10})$$

which can be diagonalized by making the substitution

$$\begin{aligned} a_k^\dagger &= u_k \alpha_k^\dagger + v_k \beta_k & a_{-k}^\dagger &= u_k \beta_k^\dagger + v_k \alpha_k \\ a_k &= u_k \alpha_k + v_k \beta_k^\dagger & a_{-k} &= u_k \beta_k + v_k \alpha_k^\dagger \end{aligned} \quad (\text{A-11})$$

with $u_k = -\sinh(\theta_k)$, $v_k = \cosh(\theta_k)$. Thus, $v_k^2 - u_k^2 = 1$. The solution is then

$$\omega_k = \sqrt{A_k^2 - B_k^2} \quad (\text{A-12})$$

Then, for the alternating chain, in the longitudinal mode,

$$\omega_k^L = \sqrt{\alpha_0 J_0} \sqrt{\alpha_0 J_0 - J_1 \cos(kD)} \quad (\text{A-13})$$

where all the terms are as described in Equation (A-8). The spin ladder has a dispersion of

$$\omega_k^L = \sqrt{\epsilon_0 J_\perp} \sqrt{\epsilon_0 J_\perp + \frac{J_\parallel}{2} \cos(kd)} \quad (\text{A-14})$$

with terms as described in Equation (A-9).

The transverse Hamiltonians, for both alternating chain and spin ladder, have the form

$$\hat{H}^T = \sum_k \left[A_k \left(a_{-k1}^\dagger a_{k1} + a_{k1}^\dagger a_{-k1} \right) - B_k \left(a_{k1}^\dagger a_{-k1}^\dagger + a_{k1} a_{-k1} \right) \right] \quad (\text{A-15})$$

This is a form that can be diagonalized by first recognizing this as the form

$$\hat{H} = \sum_{t't'} \frac{1}{2} \alpha_{t't'} c_{tk}^\dagger c_{t'k}^\dagger + \frac{1}{2} \alpha_{t't'}^* c_{tk} c_{t'k} + \beta_{t't'k} c_{tk}^\dagger c_{t'k} \quad (\text{A-16})$$

where

$$\begin{aligned} c_{1k} &= a_{k1} \\ c_{2k} &= a_{-k1} & \alpha_{23} &= \alpha_{32} = \alpha_{14} = \alpha_{41} = B_k \\ c_{3k} &= a_{k1} & \beta_{21} &= \beta_{12} = \beta_{34} = \beta_{43} = A_k \\ c_{4k} &= a_{-k1} \end{aligned} \quad (\text{A-17})$$

This Hamiltonian, Equation (A-16), can then be diagonalized by using

$$\begin{aligned} c_t &= \sum_s (\varsigma_s u_{ts} + \varsigma_s^\dagger v_{ts}^*) \\ c_t^\dagger &= \sum_s (\varsigma_s^\dagger u_{ts}^* + \varsigma_s v_{ts}) \end{aligned} \quad (\text{A-18})$$

where u_{ts} and v_{ts} are solutions to the equations

$$\begin{aligned} \sum_{t'} (\beta_{t't'} - E_s \delta_{t't'}) u_{t's} + \sum_{t'} \alpha_{t't'} v_{t's} &= 0 \\ \sum_{t'} \alpha_{t't'}^* u_{t's} + \sum_{t'} (\beta_{t't'}^* + E_s \delta_{t't'}) v_{t's} &= 0 \end{aligned} \quad (\text{A-19})$$

which gives the eigenvalue problem

$$\begin{pmatrix} 0 & A_k & 0 & 0 & 0 & 0 & 0 & B_k \\ A_k & 0 & 0 & 0 & 0 & 0 & B_k & 0 \\ 0 & 0 & 0 & A_k & 0 & B_k & 0 & 0 \\ 0 & 0 & A_k & 0 & B_k & 0 & 0 & 0 \\ 0 & 0 & 0 & -B_k & 0 & -A_k & 0 & 0 \\ 0 & 0 & -B_k & 0 & -A_k & 0 & 0 & 0 \\ 0 & -B_k & 0 & 0 & 0 & 0 & 0 & -A_k \\ -B_k & 0 & 0 & 0 & 0 & 0 & -A_k & 0 \end{pmatrix} \begin{pmatrix} u_{1s} \\ u_{2s} \\ u_{3s} \\ u_{4s} \\ v_{1s} \\ v_{2s} \\ v_{3s} \\ v_{4s} \end{pmatrix} \quad (\text{A-20})$$

which in turn is a collection of submatrices of the form

$$\begin{pmatrix} A_k & B_k \\ -B_k & -A_k \end{pmatrix} \quad (\text{A-21})$$

The solution to Equation (A-21) gives, as in Equation (A-12),

$$\omega_k^T = \sqrt{A_k^2 - B_k^2} \quad (\text{A-22})$$

although A_k and B_k are defined differently. Specifically, for the alternating chain, the transverse dispersion is

$$\omega_k^T = \sqrt{\frac{J_0(1+\alpha_0)}{2}} \sqrt{\frac{J_0(1+\alpha_0)}{2} - \alpha_1 J_1 \cos(kD)} \quad (\text{A-23})$$

and for the spin ladder,

$$\omega_k^T = \sqrt{\frac{J_\perp(1+\epsilon_0)}{2}} \sqrt{\frac{J_\perp(1+\epsilon_0)}{2} + \frac{J_\parallel}{2} \cos(kd)} \quad (\text{A-24})$$

APPENDIX B

CALCULATION OF THE MAGNETIC SUSCEPTIBILITY OF AN ALTERNATING CHAIN AND SPIN LADDER

The magnetic susceptibility of the alternating chain and spin ladder had been considered in Chapter 3, without presenting the derivation of the susceptibility. That derivation is presented in this section. The new energy levels in a magnetic field are presented, but without the full derivation as presented in Appendix A. Then the magnetic susceptibility is calculated from the new energy levels. As in Appendix A, the alternating chain and spin ladder models are presented together due to similarities in the forms derived.

B.1 Calculation of Energy Levels with a Magnetic Field

In order to calculate the magnetic susceptibility of a material, a term must be added to the Hamiltonian representing the interaction of the material with the magnetic field. With that term, the Hamiltonian for the alternating chain becomes

$$\begin{aligned} \hat{H} = \sum_l J_0 & \left[S_1^z(l)S_2^z(l) + \frac{\alpha_0}{2} (S_1^+(l)S_2^-(l) + S_1^-(l)S_2^+(l)) \right] \\ & + J_1 \left[S_2^z(l)S_1^z(l+1) + \frac{\alpha_1}{2} (S_2^+(l)S_1^-(l+1) + S_2^-(l)S_1^+(l+1)) \right] \\ & + g\mu_B H (S_1^z(l) + S_2^z(l)) \end{aligned} \quad (B-1)$$

where μ_B is the Bohr magneton, g is the Landé g -factor, and H is the magnetic field. In the same fashion, the Hamiltonian for the spin ladder is

$$\begin{aligned}
\hat{H} = & \sum_l J_{\perp} \left(S_1^z(l) S_2^z(l) + \frac{\epsilon_0}{2} (S_1^+(l) S_2^-(l) + S_1^-(l) S_2^+(l)) \right) \\
& + J_{\parallel} \left(S_1^z(l) S_1^z(l+1) + \frac{\epsilon_1}{2} (S_1^+(l) S_1^-(l+1) + S_1^-(l) S_1^+(l+1)) \right) \\
& + J_{\parallel} \left(S_2^z(l) S_2^z(l+1) + \frac{\epsilon_1}{2} (S_2^+(l) S_2^-(l+1) + S_2^-(l) S_2^+(l+1)) \right) \\
& + g\mu_B H (S_1^z(l) + S_2^z(l))
\end{aligned} \tag{B-2}$$

with terms as in the alternating chain.

As in the previous section, the Hamiltonian is converted to the pseudo-boson operators, and Fourier transformed. For the alternating chain, the resulting Hamiltonian is

$$\begin{aligned}
\hat{H}^{BL} = & \sum_k \left(\alpha_0 J_0 - \frac{J_1}{2} \cos(kD) \right) a_k^{\dagger} a_{-k} - \frac{J_1}{2} \cos(kD) (a_k^{\dagger} a_{-k}^{\dagger} + a_k a_{-k}) \\
\hat{H}^{BT} = & \sum_k \left(\frac{J_0(1+\alpha_0)}{2} - \frac{J_1\alpha_1}{2} \cos(kD) + g\mu_B H \right) (a_{-k1}^{\dagger} a_{k1}^{\dagger} + a_{k1}^{\dagger} a_{-k1}) \\
& + \frac{J_1\alpha_1}{2} \cos(kD) (a_{k1}^{\dagger} a_{-k1}^{\dagger} + a_{k1} a_{-k1})
\end{aligned} \tag{B-3}$$

and the spin ladder is

$$\begin{aligned}
\hat{H}^{BL} = & \sum_k \left(\epsilon_0 J_{\perp} + J_{\parallel} \cos(kd) \right) a_k^{\dagger} a_{-k} - \frac{J_{\parallel}}{2} \cos(kd) (a_k^{\dagger} a_{-k}^{\dagger} + a_k a_{-k}) \\
\hat{H}^{BT} = & \sum_k \left(\frac{J_{\perp}(1+\epsilon_0)}{2} + J_{\parallel}\epsilon_1 \cos(kd) + g\mu_B H \right) (a_{-k1}^{\dagger} a_{k1}^{\dagger} + a_{k1}^{\dagger} a_{-k1}) \\
& - J_{\parallel}\epsilon_1 \cos(kd) (a_{k1}^{\dagger} a_{-k1}^{\dagger} + a_{k1} a_{-k1})
\end{aligned} \tag{B-4}$$

In both cases, the longitudinal term is unchanged by the addition of a magnetic field, while the transverse term has a change in the A_k term of Equation (A-22).

The resulting dispersion is unchanged in the longitudinal term. The transverse dispersion for the alternating chain is

$$\omega_k^T = \sqrt{\frac{J_0(1+\alpha_0)}{2}} \sqrt{\frac{J_0(1+\alpha_0)}{2} - \alpha_1 J_1 \cos(kD)} \pm g\mu_B H \quad (\text{B-5})$$

and the dispersion for the spin ladder is

$$\omega_k^T = \sqrt{\frac{J_\perp(1+\epsilon_0)}{2}} \sqrt{\frac{J_\perp(1+\epsilon_0)}{2} + \frac{J_\parallel}{2} \cos(kd)} \pm g\mu_B H \quad (\text{B-6})$$

The effect of the magnetic field, then, is to split the transverse mode, while leaving the longitudinal mode intact.

B.2 Calculation of Magnetic Susceptibility

The magnetic susceptibility of the materials can be calculated given the dependence of the dispersion on the magnetic field. This was shown in Chapter 3 for the isolated dimer case, but the more complex cases will be shown here.

The magnetization of an energy level is given by

$$M_n = -\frac{d\omega}{dH} \quad (\text{B-7})$$

where M_n is the magnetization of a level, ω is the dispersion, and H is the magnetic field. Both the alternating chain and the spin ladder have two modes with non-zero magnetization, and both are identical. Specifically,

$$M_{\pm 1} = \mp g\mu_B \quad (\text{B-8})$$

The total magnetization of a material is a weighted average over the available energy levels,

$$M = \frac{\sum_n M_n e^{-\beta\omega_n}}{\sum_n e^{-\beta\omega_n}} \quad (\text{B-9})$$

where ω_n is the dispersion for the n^{th} mode, and $\beta = 1/kT$.

$$M = g\mu_B \frac{-2e^{-\beta\sqrt{\frac{J_0(1+\alpha_0)}{2}}\sqrt{\frac{J_0(1+\alpha_0)}{2}-\alpha_1 J_1 \cos(kD)}} \sinh(\beta g\mu_B H)}{1 + 2e^{-\beta\sqrt{\frac{J_0(1+\alpha_0)}{2}}\sqrt{\frac{J_0(1+\alpha_0)}{2}-\alpha_1 J_1 \cos(kD)}} \cosh(\beta g\mu_B H) + e^{-\beta\sqrt{\alpha_0 J_0}\sqrt{\alpha_0 J_0 - J_1 \cos(kD)}}} \quad (\text{B-10})$$

and for the spin ladder,

$$M = g\mu_B \frac{-2e^{-\beta\sqrt{\frac{J_\perp(1+\epsilon_0)}{2}}\sqrt{\frac{J_\perp(1+\epsilon_0)}{2}+\frac{J_\parallel}{2}\cos(kd)}} \sinh(\beta g\mu_B H)}{1 + 2e^{-\beta\sqrt{\frac{J_\perp(1+\epsilon_0)}{2}}\sqrt{\frac{J_\perp(1+\epsilon_0)}{2}+\frac{J_\parallel}{2}\cos(kd)}} \cosh(\beta g\mu_B H) + e^{-\beta\sqrt{\epsilon_0 J_\perp}\sqrt{\epsilon_0 J_\perp + \frac{J_\parallel}{2}\cos(kd)}}} \quad (\text{B-11})$$

The similarities between the two forms of magnetization are obvious. The occupation of the energy levels is different in the two, but the variation with H is the same.

The magnetic susceptibility can be obtained directly from the magnetization by

$$\chi = \frac{dM}{dH} \quad (\text{B-12})$$

where χ is the magnetic susceptibility. As the formulae are lengthy, the energy levels will not be written out, but replaced by ω_L and ω_T , representing the dispersion without the presence of a magnetic field. These are the formulae from Equations (A-13), (A-14), (A-23), and (A-24). The susceptibility is then, in both cases,

$$\begin{aligned} \chi(H, T) = & \beta g^2 \mu_B^2 \frac{-2e^{-\beta\omega_T} \cosh(\beta g\mu_B H)}{1 + 2e^{-\beta\omega_T} \cosh(\beta g\mu_B H) + e^{-\beta\omega_L}} \\ & + \beta g^2 \mu_B^2 \frac{4e^{-2\beta\omega_T} \sinh^2(\beta g\mu_B H)}{(1 + 2e^{-\beta\omega_T} \cosh(\beta g\mu_B H) + e^{-\beta\omega_L})^2} \end{aligned} \quad (\text{B-13})$$

This similarity in form is the reason the static magnetic susceptibility for the alternating chain and spin ladder cannot be differentiated. For proper choice of exchange parameters, the susceptibility can be made to match exactly.

APPENDIX C

ATOMIC POSITIONS IN THE $(\text{VO})_2\text{P}_2\text{O}_7$ UNIT CELL

The positions of the atoms in the $(\text{VO})_2\text{P}_2\text{O}_7$ molecule were found in an experiment detailed in Section 5.2. The positions are detailed below in Table C-1. The positions of the vanadium ions were not refined, due to the low scattering length of vanadium in neutron scattering. At the resolution used in this experiment, the oxygen atoms had to be refined in conjunction with the phosphorus atoms, and so the error for the oxygen atoms is not shown in this table.

Table C-1 Atomic Positions in VOPO

Atom	x (frac.)	y (frac.)	z (frac.)
V	0.2973	0.0958	0.4912
V	0.2039	0.596	0.4909
V	0.2087	0.90558	0.5023
V	0.2923	0.4057	0.5017
V	0.2055	0.8452	0.9995
V	0.2935	0.3453	0.9998
V	0.2081	0.1561	0.9986
V	0.2914	0.65607	0.9979
P	0.301(21)	1.107(14)	0.951(16)
P	0.151(21)	0.472(12)	0.777(16)
P	0.319(21)	0.248(12)	0.322(20)
P	0.355(19)	0.279(11)	0.232(21)

Table C-1 -- Continued

Atom	x (frac.)	y (frac.)	z (frac.)
P	0.223(20)	0.767(10)	0.736(18)
P	0.272(22)	0.290(11)	0.676(20)
P	0.254(23)	0.693(9)	0.419(19)
P	0.308(22)	0.236(11)	0.329(18)
O	0.5014	0.5914	0.5399
O	0.9976	0.0933	0.5397
O	0.005	0.9096	0.5313
O	0.496	0.4121	0.532
O	0.999	0.8403	0.0131
O	0.5	0.3435	0.0115
O	0.9998	0.1599	0.0125
O	0.5	0.6595	0.0108
O	0.4975	0.9986	0.8272
O	0.0044	0.4983	0.8252
O	0.496	0.7838	0.2871
O	0.0066	0.2846	0.2862
O	0.3007	0.1734	0.6421
O	0.2017	0.6734	0.641
O	0.2133	0.1761	0.3613
O	0.2943	0.6756	0.36
O	0.281	0.001	0.6307
O	0.22	0.5007	0.63
O	0.2221	0.0017	0.3639
O	0.276	0.5012	0.3619

Table C-1 -- Continued

Atom	x (frac.)	y (frac.)	z (frac.)
O	0.286	0.8205	0.6294
O	0.2117	0.3207	0.6287
O	0.199	0.8228	0.3578
O	0.298	0.323	0.3572
O	0.2659	0.0775	0.1395
O	0.2355	0.5768	0.139
O	0.2274	0.0749	0.8545
O	0.2809	0.5743	0.8535
O	0.2727	0.9246	0.1391
O	0.2329	0.4247	0.139
O	0.2234	0.9232	0.8487
O	0.2823	0.4233	0.8486
O	0.251	0.7496	0.1328
O	0.255	0.2497	0.1352
O	0.2496	0.7518	0.8606
O	0.2535	0.2517	0.8618

The chart in Table C-1 shows the fractional position of the atoms, relative to the unit cell. The unit cell parameters for VOPO are given in Section 5.1 of the text.

BIOGRAPHICAL SKETCH

Andrew Garrett was born March 23, 1967, in Dover, Delaware. He grew up in New Jersey, where he attended public schools until dropping out of high school in 1984 to attend college. He attended Cornell University, under an Air Force Reserve Officer Training Corps scholarship. After four years, he attained a degree with a triple major in Math, Physics, and Computer Science. He joined Kappa Delta Rho fraternity, and served one year as the vice president of the Cornell Intrafraternity Council.

After graduation in 1988, he attended the University of Florida to begin work on a doctorate in Physics. After one semester, he began serving in the Air Force as a condition of his undergraduate scholarship. He was sent to Texas A&M University for one year to study Meteorology, and then became the Wing Weather Officer at Malmstrom Air Force Base in Montana. During Operation Desert Storm, he was sent on deployment where he served as Squadron Weather Officer for the 1706th Air Refueling Squadron in Mont de Marsan, France, and then as Commander of Detachment 24, 1690th Weather Group in Cairo, Egypt. Upon returning to the United States, he applied for and was granted an early release from service, in order that he could return to his doctoral program. He earned a Commendation Medal, along with the Southwest Asian Campaign Medal, for his time in the military.

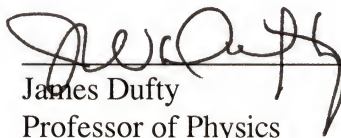
He returned to the University of Florida in 1992, and resumed his interrupted studies. He did extensive work at the National Synchrotron Light Source at Brookhaven National Laboratory. In 1996 he moved to Oak Ridge National Laboratory in Tennessee to complete his thesis research at the High Flux Isotope Reactor.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



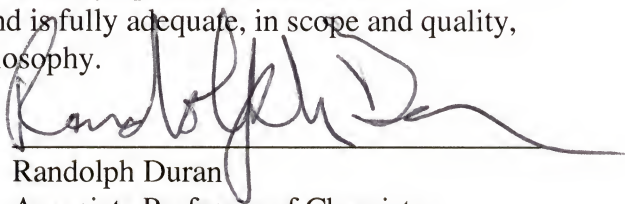
Stephen Nagler, Chairman
Professor of Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



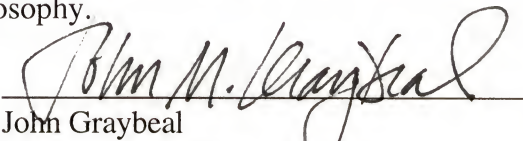
James Dufty
Professor of Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Randolph Duran
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



John Graybeal
Associate Professor of Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

A handwritten signature in dark ink, appearing to read "David B. Tanner", is written over a horizontal line.

David Tanner
Professor of Physics

This thesis was submitted to the Graduate Faculty of the Department of Physics in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May, 1998

Dean, Graduate School